Department of Forest Products Technology

Isolation of birch xylan as a part of pulping-based biorefinery

Lidia Testova

Aalto University

DOCTORAL DISSERTATIONS

Aalto University publication series
DOCTORAL DISSERTATIONS 208/2014

Isolation of birch xylan as a part of pulping-based biorefinery

Lidia Testova

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Technology, at a public examination held at the Auditorium of the Department of Forest Products Technology on the 30th of January 2015 at 12 noon.

Aalto University
School of Chemical Technology
Department of Forest Products Technology

Supervising professor
Professor Herbert Sixta

Thesis advisor
Professor Herbert Sixta

Preliminary examiners
Professor Stefan Willför, Åbo Akademi University, Finland
Professor Bodo Saake, University of Hamburg, Germany

Opponent
Associate Professor Dmitry Evtuguin, University of Aveiro, Portugal

Aalto University publication series
DOCTORAL DISSERTATIONS 208/2014

ISBN 978-952-60-6015-6 (printed)
ISBN 978-952-60-6016-3 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)
http://urn.fi/URN:ISBN:978-952-60-6016-3

Unigrafia Oy
Helsinki 2014

Finland

441 697
Printed matter

Aalto University

Abstract

Aalto University, P.O. Box 11000, FI-00076 Aalto www.aalto.fi

Author
Lidia Testova

Name of the doctoral dissertation
Isolation of birch xylan as a part of pulping-based biorefinery

Publisher School of Chemical Technology

Unit Department of Forest Products Technology

Series Aalto University publication series DOCTORAL DISSERTATIONS 208/2014

Field of research Biorefineries

Manuscript submitted 11 September 2014 **Date of the defence** 30 January 2015

Permission to publish granted (date) 18 November 2014 **Language** English

☐ **Monograph** ☒ **Article dissertation (summary + original articles)**

Abstract

This study combines various aspects of xylan isolation from birch wood as part of a pulping-based biorefinery concept. Acidic prehydrolysis and alkaline pre-extraction are the two processes used as the starting point of the work.

Solutions of xylan with diverse macromolecular and chemical properties were obtained by applying different pre-treatments. Pre-extraction at high alkalinity produced water-insoluble xylan with a high molar mass and low polydispersity. Autohydrolysis at a mild intensity yielded a liquid phase containing a variety of xylooligosaccharides and xylan of low molar mass. The fragments were mainly acetylated and some of them carried 4-O-methylglucuronic acid substituents. Intensification of autohydrolysis promoted formation of monomeric xylose and its degradation products. The addition of oxalic acid increased the monomeric fraction even at mild prehydrolysis intensities.

The properties of cellulose in the wood residue were affected to a smaller or greater extent depending on the type and intensity of the pre-treatment. After alkaline pre-extraction at low temperature and high alkalinity, the macromolecular properties of cellulose were barely affected. After mild prehydrolysis, cellulose was partly depolymerised without a notable yield loss. When more severe prehydrolysis conditions were applied, as required for an almost complete removal of hemicelluloses, both the degree of polymerisation and yield of cellulose were affected dramatically.

An attempt to mitigate gradual cellulose degradation induced in the pulping stage by prehydrolysis was made with cotton linters as a cellulose substrate. Sodium borohydride and different types of anthraquinone (AQ) were able to convert a share of the reducing end groups to either alditol or aldonic acid moieties stable to alkaline peeling. Such stabilisation had a positive effect on the yield of cellulose. Stabilisation was also reflected in the decreased ratios between the peeling and stopping reaction rate constants. An improved model for cellulose degradation in alkaline environments was developed that took secondary peeling into account. Application of the stabilisation chemicals to birch wood resulted in a moderate yield increase and the preferred stabilisation of hemicelluloses.

Aqueous-phase prehydrolysis of birch wood followed by alkaline pulping produced dissolving pulps of viscose and acetate quality without alkaline post-extraction. Changes of cellulose crystallite dimensions and specific surface area between microfibril aggregates in bleached pulps were observed as functions of prehydrolysis intensity. Mild oxalic acid prehydrolysis and alkaline pre-extraction were shown to be well suited the production of paper pulps, where the latter pre-treatment ensured excellent papermaking properties.

Keywords alkaline pre-extraction, birch, prehydrolysis, pulping, xylan

ISBN (printed) 978-952-60-6015-6 **ISBN (pdf)** 978-952-60-6016-3

ISSN-L 1799-4934 **ISSN (printed)** 1799-4934 **ISSN (pdf)** 1799-4942

Location of publisher Helsinki **Location of printing** Helsinki **Year** 2014

Pages 164 **urn** http://urn.fi/URN:ISBN:978-952-60-6016-3

It is truly inspiring that beings confined to one planet orbiting a run-of-the-mill star in the far edges of a fairly ordinary galaxy have been able, through thought and experiment, to ascertain and comprehend some of the most mysterious characteristics of the physical universe.

Brian Greene
from "The Elegant Universe"

Preface

The work summarised in this thesis was carried out at Helsinki University of Technology and now Aalto University, from 2009–2014.

First and foremost, I would like to thank my supervisor and teacher Professor Herbert Sixta. Your kind offer for me to come to Finland and join a very young-at-the-time research group literally changed my whole life. Your careful guidance and enthusiasm made this work possible.

The largest share of this study was performed as part of the HemiEx Project. I am grateful to Tekes – the Finnish Funding Agency for Innovation, and to Andritz Oy, Danisco, Metsä Fibre Oy, Stora Enso Oyj, and UPM for the financial support, in-kind contribution and fruitful discussions. My research partners at Aalto University, the University of Helsinki and Lappeenranta University of Technology are thanked for their excellent collaboration.

I would like to express my deepest gratitude to BIOREGS – the Doctoral Programme for Biomass Refining, the Paper Engineers' Association and the Walter Ahlström Foundation for providing additional financial support essential for finalising this thesis.

I would also like to sincerely thank all of my co-authors. Professor Maija Tenkanen, an adorable person with lots of enthusiasm and a great sense of humour, your presence lit up every research meeting and your excellent comments on the manuscripts often made me think outside the box. Sun-Li Chong with the deepest expertise in MALDI-TOF MS technique guided me through this complex experiment (only later did I understand how it really works). Professor Antje Potthast astounded me with the most advanced analytical techniques and with her kind personality. Kaarlo Nieminen developed a mathematical model that became a centrepiece of Paper II, and always had time for answering my stupid and hopefully sometimes-more-reasonable questions. English and Mathematics were my favourite subjects at school, but I would not even dream of developing complicated mathematical models to describe what was happening in small autoclaves as you do! Dr. Paavo Penttilä's knowledge and hard work helped me to not only complement my experiments with "fancy" data but helped me to better understand the complicated (and controversial) world of cellulose structures. And yes, I also imagined you differently before I met you for the very first time! Professor Ritva Serimaa, you always willingly supported our collaboration, from which I hope your research group also benefited. Dr. Marc Borrega became a real role model for me. When you joined our group, you showed how true passion for research can make one an expert in something totally new in no time. Moreover, you have never been in bad mood and always cheered me up when the results did not make much sense. Lasse Tolonen – the guru of GPC and all the other fancy things – contributed to this thesis much more significantly than could be seen at first. You gave loads of polymer-related advice and even shared my interest in visiting the National Air and Space Museum in Washington, D.C.! Luciana Costabel, with your outstanding diligence and an endlessly kind heart, you brought something very special to this work. Annariikka Roselli – simply an amazing person in all respects – you were responsible not only for my decision to create Paper IV but also often for my mental health, for which I thank you! Dr. Kari Kovasin, you always provided me with the best

advice, shared your broad expertise and were a perfect listener, even when you had to listen to me at airports for too many hours.

Without all of you this journey would not be as great, and I thank each one of you for joining me in this work.

I am also grateful to Dr. Agnes Stepan for reading this thesis I do not know how many times and always finding ways to improve it. You did an absolutely excellent job with my far-from-excellent writing!

The most important part of our research always happens in a laboratory. I would like to thank everybody who provided me with their highly qualified support in the lab. Rita Hatakka, Heikki Tulokas, Myrtel Kål, Maarit Niemi, Ritva Kivelä, Anu Anttila, Christian Orassaari, Tuyen Nguyen, Minna Mäenpää and Mikaela Trogen: you saved me from many tears and made my life less miserable. On top of that, you were good company in the lab and often made me smile! Seppo Jääskeläinen, Timo Ylönen and the workshop group are warmly thanked for the invaluable help with the equipment, which they always provided without any delay. Seppo, I would like to particularly thank you for selflessly spending hours and days next to the 10L-reactor with me!

One of the newest and most exciting things I learnt about in connection with this work was cellulose acetate production. Therefore, I would like to express my gratitude to Dr. Armin Stein and Solvay Rhodia for accepting me into their facility in Freiburg im Breisgau and guiding me through the world of cellulose acetate. This was invaluable!

All the former (Riitta Hynynen, Ursula Klemetti, Anne Jääskeläinen, Anne Forsström) and current (Sirje Liukko, Ritva Vuorinen, Iina Leporanta-Varjus, Hannele Taimio, Jenni Ala-Hongisto, Saija Helasuo, Esther Koskinen, Tuire Mikluha-Koskinen, Heli Järvelä) support team members are thanked for their great efforts, which made my work very smooth. Special appreciation goes to Mao Naomi Ohno♥, whose light and whose unbelievable ability to work inspired me every day. Mao, I cannot put in words how much you mean to me!

I would like to thank Pentti Risku for the always-timely and efficient IT support, and Kati Mäenpää and Lilija Stelmahova for their help with books and journals. I needed your assistance very often and you were always ready to provide it. Ari Häkkinen and Timo Jokinen, you also provided me with essential practical help.

I am grateful to all of the students who contributed to my project: Helena Moring, Ziniu (Neo) Wu, Yibo Ma, and Mikko Suhonen. In particular, I would like to thank Mikko Leppikallio and Marianthi Elmaloglou, who contributed to this thesis with their hard work in the lab.

My “group thanks” are addressed to the “HemiEx girls” (in order of their appearance): Tiina Rauhala, Luciana Costabel, Marina Alekhina, Annariikka Roselli and Olga Ershova. It was a splendid time and a successful project, hasn’t it?

Many thanks to Professor Adriaan van Heiningen for your humanity and your ability to inspire; I am so glad to have got to know you! I would also like to acknowledge Professor Tapani Vuorinen and Professor Janne Laine for taking such good care of our department and always helping when it was needed.

I am extremely glad to have met everyone on our research team, particularly (in random order) Dr. Michael Hummel, Lauri Hauru, Markus Paananen, Yibo Ma, Xiang You, Dr. Minna Yamamoto, Dr. Hanna Hörhammer, Dr. Evangelos Sklavounos, Vahid Jafari, Terhi Toivari, Ville Ali-Rekola, Pertti Korppi, Dr. Kyösti Ruuttunen, Marmar Ghorbani, Anne Michud, and also many people on other research teams: Elli Niinivaara, Dr. Laura Taajamaa, Dr. Tiina Nypelö, Dr. Anna Olszewska, Dr. Miro Suchy, Dr. Katri Kontturi, Dr. Eero Kontturi, Dr. Marcelo Muguet, Delphine Miquel, Akio Yamamoto, Dr. Ilari Filpponen (thank you for the reducing ends!), Dr. Raili Pönni, Kari Vanhatalo, Heikki Hannukainen and Asko Koskimäki. It has been a pleasure to work under the same roof with you all.

Marina Alekhina and Olga Ershova, you started in the HemiEx project, and my "motherly" feelings towards you both are still alive! Girls, it has been awesome having lunches and attending events together, and discussing all the different things in the world, from analytical methods to peculiarities of language vocabulary in neighbouring and distant regions of Russia. Everybody else: sorry for the noise! I hope we can keep doing all of this (including the noise) for many years, at least now and then. Don't forget to visit my "village"…

I would like express appreciation to my friends, colleagues and absolutely incredible people ("incredible" in the Longman Dictionary of Contemporary English: 1. extremely good, 2. too strange to be believed), Dr. Mikhail Iakovlev and Dr. Niko Aarne. With you I spent absolutely unforgettable times in PUU1 and in different corners of Finland and the world. Those times will always remain in my heart as a benchmark of how my life in Finland started. Crazy, eh?

Niko, thank you for your unbelievable ideas, big heart, great command of Russian language, love of board games, passion for dancing, and the best SAAB in the world!

Misha, I am truly grateful to you for being my helping hand upon first request, for the hours in the labs together (remember, sometimes until 5 in the morning?) and thousands of kilometres on our bikes, for the music and candies, cheese and tea without tea… I have known you for 15 years – thank you for always being there!

Seppo Pursiainen is warmly acknowledged for offering his apartment (free of rent!) for undisturbed use in the summer of 2009. Sepushka, you really saved me! Laila Hosia is thanked for considering me a suitable lodger for her lovely apartments in Nallenpolku and for the nice evening conversations.

I would like to express endless gratitude to "The Swedish Family", our little "home chemical society" (in alphabetical order) Dr. Christian Andersson, Dr. Danil Korelskiy, Katya Avershina, Katya Petrova, Oleg Agafonov, Tanya Ruksha, Tonya Lobanova and Vanya Bykov. You always believed in me, and you were my true inspiration in this work. This is more than just friendship.

Many thanks to all of my friends outside Finland for staying in my life and keeping me "normal" for all these years. Tanya P. & Eskil H., Anya O. & Sergey O., Kostya T., Ira K., Stas B., Marina N., Lida G. and Ilya R., I appreciate you all!

Любимые мама и папа, спасибо вам за то, что вы есть! Лучшей семьи и быть не может!

Taavi, I met you when I needed it the most, and your love and care made my life full. You helped me to dream my dreams and fulfil my accomplishments. You also made me dream new dreams, some of which you have already fulfilled for me. You involved me in all of your unconventional hobbies and let me be a part of your family and your circles. Thank you for everything!

Finally, our toyger cat Osama is acknowledged for never caring about the science but contributing to the writing with all four of his paws!

Espoo, November 2014

Lidia Testova

List of publications

Paper I

Lidia Testova, Sun-Li Chong, Maija Tenkanen and Herbert Sixta. 2011. Autohydrolysis of birch wood: 11th EWLP, Hamburg, Germany, August 16-19, 2010. *Holzforschung*. 65, 535-542.

Paper II

Lidia Testova, Kaarlo Nieminen, Paavo A. Penttilä, Ritva Serimaa, Antje Potthast and Herbert Sixta. 2014. Cellulose degradation in alkaline media upon acidic pretreatment and stabilisation. *Carbohydrate Polymers*. 100, 185-194.

Paper III

Lidia Testova, Marc Borrega, Lasse K. Tolonen, Paavo A. Penttilä, Ritva Serimaa, Per Tomas Larsson and Herbert Sixta. 2014. Dissolving-grade birch pulps produced under various prehydrolysis intensities: quality, structure and applications. *Cellulose*. 21(3), 2007-2021.

Paper IV

Lidia Testova, Annariikka Roselli, Luciana Costabel, Kari Kovasin, Maija Tenkanen and Herbert Sixta. 2014. Combined production of polymeric birch xylan and paper pulp by alkaline pre-extraction followed by alkaline cooking. *Industrial & Engineering Chemistry Research*. 53(9), 8302-8310.

Author's contribution

I Lidia Testova was responsible for the experimental design, performed the major part of the experimental work, analysed the results together with the co-authors and wrote the manuscript as principal author.

II Lidia Testova was responsible for the experimental design, performed the major part of the experimental work, analysed the results using the degradation model developed by Kaarlo Nieminen and wrote the manuscript as principal author.

III Lidia Testova participated in the experimental design and performed the experimental work together with the co-authors, analysed the corresponding results and wrote the manuscript as principal author.

IV Lidia Testova participated in the experimental design together with the co-authors, performed evaluation of papermaking properties and part of chemical analyses, analysed the results and wrote the manuscript as principal author.

List of essential abbreviations

AQ – anthraquinone

AQS – AQ monosulfonic acid sodium salt

BH – sodium borohydride

CL – cotton linters

DP – degree of polymerisation

DS – degree of substitution

E-SAQ – pre-extraction soda AQ process

HMF – hydroxymethyl furfural

MeGlcA – 4-*O*-methylglucuronic acid

MSA – metasaccharinic acid

OA – oxalic acid

o.d. – oven-dry

P – prehydrolysis

REG – reducing end-group

SAQ – soda AQ

XOS – xylooligosaccharides

Table of contents

1. Introduction and outline of the study

The principle of biorefinery is focused on sustainable fractionation and conversion of biomass components into products. Wood xylan is seen as a potential raw material for a variety of value-added end products. Integrating xylan isolation into an existing pulp production process chain is a promising industrial approach. Water prehydrolysis and alkaline extraction – both known and extensively studied processes – have not yet been widely commercialised due to a number of challenges and open questions. The aim of this work was to investigate some aspects which had not been studied in depth in previous research. Birch wood (*Betula pendula*) was selected for the experiments due to its exceptionally high content of xylan. Despite the fact that birch is the most abundant hardwood species in the Nordic countries, it has been relatively neglected in recent studies. In Finland 20% of all forest resources are represented by hardwoods, of which 85% are reported to be birch (Metla Finnish Forest Research Institute, 2009).

In the present work, special emphasis was placed on fractionation of birch wood aimed at the recovery of pure xylan- and cellulose-based products for further valorisation routes. Fractionation was performed by autohydrolysis, oxalic-acid catalysed prehydrolysis, or alkaline pre-extraction followed by alkaline pulping. First, autohydrolysis was studied in detail in **Paper I**, in which the overall mass balance of the process was the focus of the work at two prehydrolysis intensity levels, potentially suitable for paper- and dissolving-grade pulp production. The changes in the properties of xylan in the wood residue as well as the chemical and macromolecular composition of the liquid phase were monitored. Despite the negligible cellulose yield loss in the solid wood residues, depolymerisation of cellulose as a result of hydrolytic attack in the acidic environment was anticipated. Due to the cleavage of glycosidic bonds new reducing end-groups (REG) are generated which cause beta-elimination reactions in a subsequent alkaline cooking that lead ultimately to yield losses. Such degradation and the possibilities of minimising it were therefore studied by means of stabilisation in **Paper II**. In order to avoid the effects of other wood components, cotton was selected as a model substrate for the study. The cellulose yield loss characteristics and the behaviour of the functional groups at the reducing end upon the addition of stabilisation chemicals were studied in detail. An improved model for cellulose degradation that included secondary peeling at the newly-generated REG was also developed. In **Paper III,** a wider range of autohydrolysis intensities prior to soda-anthraquinone (SAQ) cooking was applied to produce dissolving pulps aimed at the

specifications of viscose and acetate grades. The efforts were focused on investigating the chemical, macromolecular, and structural properties of the obtained bleached pulps and testing their suitability for dissolving pulp applications. Oxalic acid prehydrolysis of birch wood as an alternative to autohydrolysis for the production of paper pulps was also studied. This work is included here with a reference to **Testova et al. (2012a)**. Oxidative and reductive stabilisation techniques were both applied to the wood residue after oxalic acid prehydrolysis.

Paper IV focused on alkaline pre-extraction of birch wood at moderate temperatures and high alkalinity in the absence of a nucleophile. For the alkaline process, a holistic approach was applied to study a potential process chain from the optimisation of pre-extraction to final products. Production of a paper pulp from the pre-treated wood was complemented by the separation and purification of the extracted xylan. Model experiments to produce xylooligosaccharides (XOS) by enzymatic hydrolysis were performed, and the economic potential of alkaline pre-extraction was discussed.

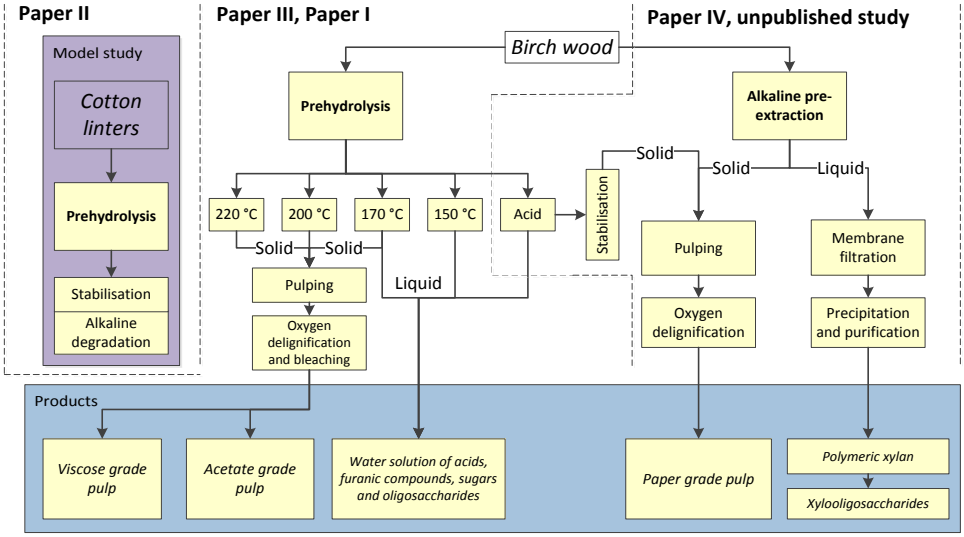

Figure 1. The experimental outline of the thesis. Two pre-treatment types were applied to birch wood and were followed by analytical characterisation of the products. Fractions of the selected pre-treatments were converted to pulps and hemicellulose products. Effect of prehydrolysis on cellulose retention in alkaline pulping was investigated in the model study.

This work is motivated by the current demand in the forestry industry for more sustainable utilisation of biomass. An in-depth understanding of biomass fractionation processes is a prerequisite for designing and implementing biorefinery concepts. Developing a solution toolkit that addresses process challenges is an important step towards actualising future biorefineries.

2. Background

2.1 Biorefinery concepts

A biorefinery has been defined by the National Renewable Energy Laboratory (NREL) as "a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass" (NREL, 2009). Biomass in this instance is defined as biological material derived from plants, and is also referred to as lignocellulosic material. The basic principles of biomass fractionation and conversion were developed decades ago. Ragauskas et al. (2006) and Dodds and Gross (2007) pointed out that at the beginning of the 20th century, a high percentage of chemicals and materials was manufactured from renewable resources until they were replaced by cheaper petroleum-based equivalents in 1970s. Later, the interest in biomass resources was highly stimulated by petroleum's low availability and high prices. At the beginning of the twenty-first century, biorefinery-related activities gained momentum on a global level. The awareness of the anthropogenic impact on global climate change has been a key driving force for this development (Bernstein et al., 2007), though an increase in global energy demand combined with declining conventional energy resources has played an important role (Kurian et al., 2013). Current trends in fractionation and conversion of biomass have been described by a wide number of scholars, including Ragauskas et al. (2006), Clark et al. (2006), Demirbas (2009), FitzPatrick et al. (2010), Menon and Rao (2012), Clark et al. (2012), Zhang (2013), Gravitis and Abolins (2013), Kurian et al. (2013), Hughes et al. (2013), and Kamm (2014).

In general terms, biorefinery, like oil refinery, implicates fractionation of the raw material into individual compounds or groups of compounds of a similar nature. Thermal conversion of biomass to products partially or completely omitting the fractionation step is also a part of the biorefinery framework (Demirbas, 2009). In contrast to crude oil, biomass alone is carbon-neutral as a result of photosynthesis (Ragauskas et al., 2006), is renewable, and is widely available. Consequently, bio-products typically have a much smaller net contribution of CO_2 than their oil-based equivalents (Clark et al., 2006, Clark et al., 2012). The other advantages of biomass constituents are the unique structure, chiral purity, and easy derivation of alcohols, carboxylic acids, and esters, which eliminate the tedious oxidation process (Ragauskas et al., 2006). Furthermore, biological conversion processes widely available for biomass-

derived products do not require the high temperatures and pressures demanded by the processes employed by oil refineries. On the other hand, oil refinery benefits from highly efficient, well integrated, and often continuous fractionation and conversion processes, while fractionation of biomass requires a multitude of different downstream processes for the efficient isolation and purification of the resulting products. A complex chemical structure of biomass tissues limits the availability of selective fractionation methods and has, therefore, been holding back the introduction of biorefineries as an alternative to oil refineries. Another major advantage of crude oil lies in the field of fuel production. Due to the intrinsically low oxygen content of the oil constituents, oil-based fuels typically have higher energy content per unit volume than typical biofuels.

Bozell (2010) reviewed the possibilities of using biomass-derived compounds as feedstock to existing petrochemical industry plants. Here, levulinic acid – a dehydration product of sugars – is seen as a suitable candidate for such feedstock. Suggested chemical pathways include conversion of levulinic acid to γ-valerolactone. The latter can be subsequently decarboxylated to isomeric butenes to produce mixed liquid alkenes or hydrogenated to valeric acid with further esterification possibilities. Both product groups have a potential to be used as transportation fuels.

Production of organic chemicals and materials from biomass has been given less attention than the development of alternative fuels. Dodds and Gross (2007) discussed the high potential of biomass as a raw material for a number of chemicals either currently produced or analogous to those derived from crude oil. The US Department of Energy published a 2004 report summarising the commodity chemicals, or so-called building blocks that could be produced from biomass by chemical and biological routes. The building blocks derived from carbohydrates included 1,4 succinic, fumaric and malic acids, 2,5 furan dicarboxylic acid, 3 hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol/arabinitol (Werpy et al., 2004). A number of biomass-derived products are already commercially available, including glutamic acid, citric acid, lysine, levulinic acid and polylactic acid (PLA). In addition to PLA, lactic acid can also be converted into lactate, lactide and methacrylic acid. A number of cost-effective processes have been developed to produce commodity chemicals from biomass, for example 1,3 propanediol, succinic acid, catechol and other aromatic alcohols, poly-3-hydroxyalkaloates, vanillin, duaiacol etc. (Dodds and Gross, 2007).

Cherubini et al. (2009) discussed classification of biorefineries according to four principles: platforms, products, feedstock, and processes. Platforms are the intermediates of biomass fractionation and conversion that are used as a basis for a variety of end-products. Such platforms can be divided into biogas, synthesis gas (syngas), hydrogen, C6 sugars, C5 sugars, lignin, pyrolysis liquid, oil and organic juice. These platforms can be converted into products such as transportation fuels, electricity

and heat, building block and end-use chemicals, materials, food, and feed. Dedicated crops and residues originating from agriculture, forestry, industry and households and even from aquafarming can serve as biorefinery feedstock (Hughes et al., 2013, Kurian et al., 2013). Importantly, non-food feedstocks should be preferably used for the non-food applications (Zhang, 2013).

Biorefineries exploit a variety of processes in a wide range of conditions from ambient to extreme (Cherubini et al., 2009, FitzPatrick et al., 2010, Gravitis and Abolins, 2013, Hughes et al., 2013). Figure 2.1 summarises the classes and the most common examples of such processes.

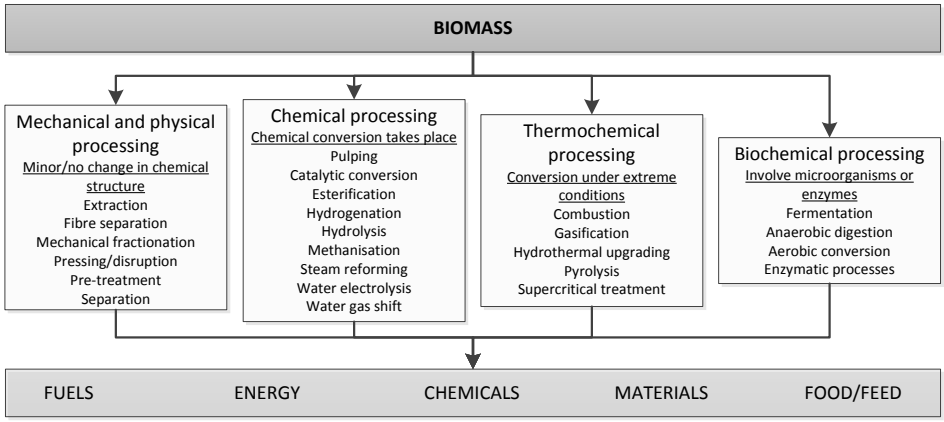

Figure 2.1. Overview of the processes exploited in biorefineries. Adopted from Cherubini et al. (2009).

Chemical pulp production facilities embody many features of a biorefinery. In a pulp mill, biomass is converted into materials, chemicals, and energy. A number of techniques, including extraction, separation, mechanical fractionation, pulping, hydrolysis, and combustion are typically combined in a sophisticated and well-established process. At present, hardwood kraft pulp manufacturers in the Northern Hemisphere are surpassed by the modern facilities in the Southern Hemisphere that benefit from low-cost feedstock, state-of-the art technologies and economies of scale. As a possible solution to the declining competitiveness, van Heiningen (2006) summarised the possibilities of developing a kraft pulp mill into an integrated forest biorefinery by a more elaborate conversion of the wood components and converting by-products into chemicals, fuels, and materials. Van Heiningen (2006) pointed out that hemicelluloses and lignin once isolated from the process streams should be converted into products with a high added value rather than combusted in a recovery boiler. Furthermore, an existing pulp mill facility compared to a new greenfield biorefinery has the advantage of an established raw material supply and infrastructure. The idea of an integrated forest biorefinery was further developed into a variety of scenarios where the pulping process is

utilised as the principal fractionation step (Fatehi and Ni, 2011b, Fatehi and Ni, 2011a, Paleologou et al., 2011, van Heiningen et al., 2011, Christopher, 2013). Engelberth and van Walsum (2012) reviewed the possibilities of adding value to the integrated forest biorefinery by isolating hemicelluloses before pulping by prehydrolysis and alkaline pre-extraction. The authors discussed commercially attractive valorisation routes of hemicelluloses into alcohols, triacylglycerides, alkanes and fermentation into commodity chemicals.

An impressive number of pilot, demonstration, and commercial biorefinery facilities have been established around the globe. So far, as pulping based biorefineries are concerned, the few remaining sulphite pulp mills have been successful in following the biorefinery concept. Unquestionably, implementing biorefinery principles based on kraft process is on its way to realisation. The examples of pulping-based facilities and their product ranges are:

Borregaard (sulphite), producing specialty cellulose, dissolving cellulose, several lignin products, fine chemicals like amino alcohols and derivatives, pharmaceutical intermediates, intermediates for X-ray contrast media, ingredients like vanillin and ethylvanillin, bioethanol, acetic acid, citric acid, etc. (borregaard.com);

Lenzing AG (sulphite), producing dissolving pulp and regenerated fibres, acetic acid, furfural, magnesium lignin sulfonate (lenzing.com);

Domsjö (sulphite), producing specialty cellulose, lignin, bioethanol (domsjo.adityabirla.com);

MeadWestvaco Corporation (kraft), offering a variety of tall oil and lignin-based chemicals, activated carbon, and asphalt additives in addition to traditional packaging materials (mwv.com);

Solander Science Park and Smurfit-Kappa Kraftliner Piteå (kraft), developing black liquor gasification and black liquor valorisation processes and valorisation of tall oil (piteasciencepark.se);

Metsä Fibre, Äänekoski (kraft), expanding with a greenfield biorefinery facility by 2017. The process is designed to produce softwood pulps and a variety of bioproducts and bio-based energy (metsagroup.com).

2.2 Hemicelluloses as a source of valuable products

The typical raw materials for pulp production – softwoods and hardwoods – differ considerably in their gross composition. While both contain similar amounts of cellulose, the share and structure of lignin and hemicelluloses are notably different (Alen, 2000a). Hemicelluloses are branched heteropolysaccharides, and they usually amount to between

20 and 30% of the dry weight of wood. These polysaccharides are composed of different monomeric sugar units such as D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose and L-rhamnose, as along with D-glucuronic, D-galacturonic and 4-*O*-methyl-D-glucuronic acids. Due to their amorphous structure and a rather low DP in wood of about 200, hemicelluloses are fairly easily hydrolysed by acids to monomers (Sjöström, 1993). Typical hemicelluloses found in softwoods are galactoglucomannans (GGM), arabinoglucuronoxylans and arabinogalactans. In hardwoods, glucuronoxylans (xylans) are by far the dominant hemicellulose type (Figure 2.2) while glucomannans and other hemicelluloses occur in much smaller amounts (Alen, 2000a).

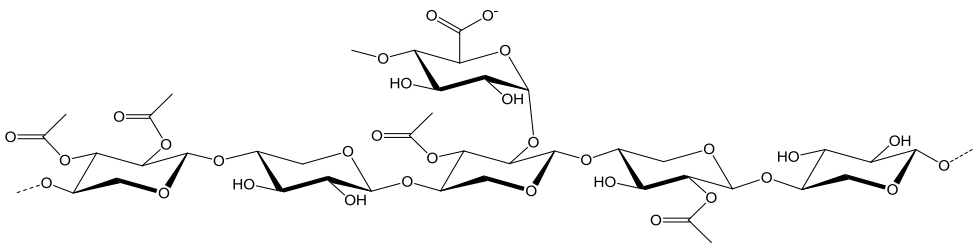

Figure 2.2. Typical structure of birch wood xylan molecule (*O*-acetyl-4-*O*-methylglucurono-β-D-xylan).

Birch wood comprises 25-28% xylan (Sjöström, 1993) of which the major component is *O*-acetyl-4-*O*-methylglucurono-β-D-xylan. The backbone consists of β-(1-4)-D-xylopyranosyl units (Sjöström, 1993), which carry α-(1→2)-linked 4-*O*-methylglucuronic acid (MeGlcA) residues, at a molar ratio of approximately 1 MeGlcA unit per 15 xylose units (Teleman et al., 2002, Pinto et al., 2005). Birch xylan is acetylated with an average degree of substitution (DS) of 0.6 (Lindberg et al., 1973, Teleman et al., 2002) with partial substitution in positions 2 (23.7 mol%), 3 (22.5 mol%) and 2, 3 (9.5 mol%), while 44.3 mol% are unsubstituted (Lindberg et al., 1973). Teleman et al. (2002) observed that the α-(1→2)-substitution with MeGlcA residues in xylans occurs preferably at the units which are acetylated in 3-*O*-positions.

Due to the unique and versatile nature and high availability potential, hemicelluloses in general and xylans in particular are an appealing raw material for numerous applications (Ebringerova et al., 2005). Xylans can be isolated from a feedstock in polymeric, oligomeric or monomeric form or as a mixture of them. Deutschmann and Dekker (2012) summarised a variety of conventional and novel applications for xylans and their depolymerisation products.

Applications of polymeric xylans from wood have thus far been limited due to the rather low degree of polymerisation (DP~200 for native xylans (Sjöström, 1993)) compared to cellulose, for example (DP up to 15 000 (Sjöström, 1993)). Nevertheless, novel products from polymeric xylans are presently in the spotlight of scientific research. Gröndahl et al.

(2004) and Escalante et al. (2012) studied the possibilities of preparing films from polymeric xylans mainly from non-wood sources. Promising features of such materials like excellent oxygen, grease and aroma barrier properties could be utilised for the production of biodegradable or even edible packaging films. Xylans can be functionalised (Alekhina et al., 2014) or combined with other carbohydrate derivatives and plasticisers (Mikkonen and Tenkanen, 2012) to achieve certain properties. The major challenges with xylan-based barrier films have been their high sensitivity to moisture and low stretchability. Furthermore, a high molar mass of xylan is required to ensure high film-forming ability. The use of plasticisers, cross-linking agents and blending polymers is seen as a potential solution for the challenges (Mikkonen and Tenkanen, 2012). Another important research focus is the formation of three-dimensional porous foams and gels from cross-linked xylans, which could find applications in cosmetics, pharmaceutics, tissue engineering, etc. (Deutschmann and Dekker, 2012, Kuzmenko et al., 2014). Further, polymeric xylans may find applications in the food industry as nutritional fibres and a water binder (Sedlmeyer, 2011), in the pharmaceutical industry as a drug delivery medium, and in the chemical industry for the production of natural biodegradable surfactants. Finally, polymeric xylans could also serve as an additive to pulp fibres to improve yield and retention of chemicals in papermaking and to strengthen some of the final product's properties, such as tensile strength and resistance to axial compression (Vaaler, 2008, Öhman and Danielsson, 2011).

Commercial production of oligomeric xylan derivatives is a recently-developed fast-growing niche (Vázquez et al., 2000) at the moment mainly present in China. To date, the most promising application of pure xylooligosaccharides (XOS) (Figure 2.3) is prebiotics (Carvalho et al., 2013). Prebiotics are indigestible food ingredients that selectively stimulate the growth and activity of certain bacterial species resident in the colon. Intake of prebiotics has a medically confirmed positive health effect (Gibson and Roberfroid, 1995). Indigestible oligosaccharides like XOS and fructooligosaccharides are known to have prebiotic effect (Gibson and Roberfroid, 1995, Aachary and Prapulla, 2011). XOS are produced as a mixture of fragments composed of xylose and possibly arabinose residues, acetylated fragments and fragments containing MeGlcA substituents. The presence of the acetyl and MeGlcA substituents in XOS prebiotic substrates slows down fermentation and results in reduced production of lactate and increased production of propionate and butyrate, as demonstrated by Kabel et al. (2002) in an in vitro experiment. MeGlcA substituents in XOS are also believed to have anti-cancerous properties, blood- and skin-related effects, anti-allergy effects, anti-infection and anti-inflammatory properties, immunomodulatory action, and anti-hyperlipidemic effects (Aachary and Prapulla, 2011). In addition to prebiotic applications, XOS after chemical functionalisation can be used in medicine, production of surfactants and cosmetics (Deutschmann and Dekker, 2012). XOS can be obtained by fractionating low molar mass biomass autohydrolysates (Vázquez et al., 2005) or by selective enzymatic or chemical

hydrolysis of polymeric xylans directly in biomass or pulp (Hakala et al., 2013) or after extraction (Griebl et al., 2005, Metsämuuronen et al., 2013).

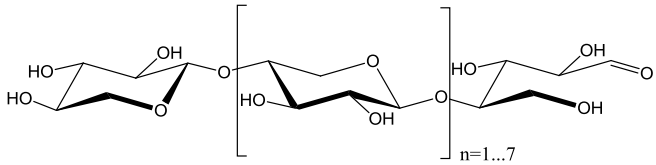

Figure 2.3. Simplified structure of neutral XOS.

Monomeric xylose, one of the platform chemicals, can be used directly as a sweetener or can be converted to xylitol by hydrogenation (Deutschmann and Dekker, 2012) (Figure 2.4). Another typical product, furfural, is produced by catalysed dehydration of xylose (Zeitsch, 2000, Karinen et al., 2011). Furfural, in turn, can be decarbonylated to furan, which is included in the list of the sugar-derived building block chemicals (Werpy et al., 2004). Alternatively, xylose can be fermented to other building block chemicals, such as succinic or dicarboxylic acid, by using genetically manipulated microorganisms (Andersson et al., 2007, Helmerius, 2010). Despite the difficulties, laborious research has also resulted in new possibilities of producing second generation bioethanol from xylose by yeast fermentation (Di Nicola et al., 2011). Finally, some xylan-derived products such as furfural and acetic acid can be recovered as by-products of parts of lignocellulose fractionation, like sulphite pulping or acidic prehydrolysis.

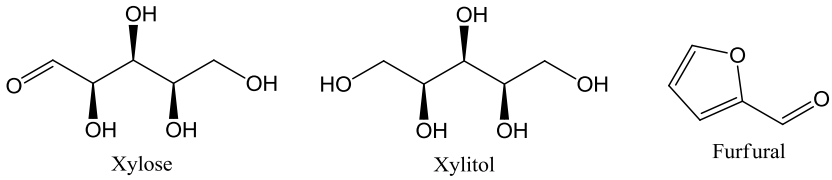

Figure 2.4. Principal commercial xylan-derived products.

At present, xylose, xylitol (Nigam and Singh, 1995), and furfural (Hoydonckx et al., 2000) are, among others, typical commercial xylan-derived products.

2.3 Isolation of xylan in a pulp mill

Historically, hemicellulose isolation was primarily attempted in the context of cellulose purification for the manufacture of dissolving pulp rather than the conversion of hemicelluloses to products. Multistage pulping processes were developed for the production of high-purity pulps to eliminate the shortcomings of single-stage processes in terms of selectivity. The first development of the prehydrolysis kraft (PHK) process occurred in Germany during World War II (Rydholm, 1964, p. 281). By the present day, a number of pathways have been described to isolate hemicelluloses from lignocellulosic feedstock in connection with alkaline pulp production (Figure 2.5).

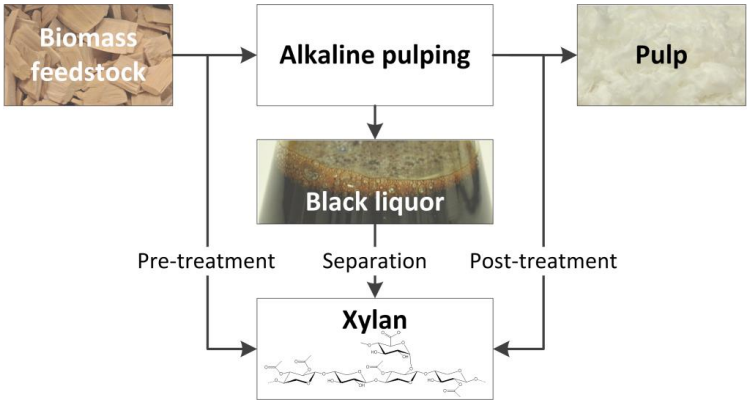

Figure 2.5. Schematic representation of the xylan-isolating possibilities in a pulp mill.

2.3.1 Prehydrolysis

Treatment of biomass in pure aqueous or acid-catalysed conditions at elevated temperatures is called prehydrolysis. The development of wood autohydrolysis and acid prehydrolysis dates back to the 1940s; those studies were related to the need to upgrade wood pulp purity in terms of hemicellulose content (Overbeck and Mülller, 1942). By the 1950s Richter could give a detailed overview of the process (Richter, 1955, Richter, 1956) in connection with alkaline pulping applied to a number of hardwood and softwood species. In prehydrolysis, temperature, acidity and duration determine the extent of the hydrolytic attack. A combination of these variables can be used as a tool to obtain various pulp properties such as hemicellulose content, degree of polymerisation (DP), and crystallinity. Prehydrolysis affects lignin retention and structure in wood and may result in the formation of condensed lignin structures when high intensities are applied. Prehydrolysis is particularly efficient in removing pentosans from hardwoods (Richter, 1955, Richter, 1956). Later, a number of research groups reported their results on various aspects of prehydrolysis. Prehydrolysis mass balances are available for a variety of wood species (Bernardin, 1958, Springer, 1985, Garrote et al., 1999a, Nabarlatz et al., 2007, Rudie et al., 2007, Tunc and van Heiningen, 2008, Leschinsky et al., 2009, Testova et al., 2009, Kämppi et al., 2010, Borrega et al., 2011a). Kinetic and mechanistic studies improved the fundamental understanding of the prehydrolysis process (Conner, 1984, Bobleter, 2004, Nabarlatz et al., 2004, Chen et al., 2010). Many studies focused on a combination of sequential prehydrolysis and pulping processes (Richter, 1955, Richter, 1956, Kerr et al., 1976, Schild et al., 1996, Testova, 2006, Al-Dajani et al., 2009, Kämppi et al., 2010, Schild et al., 2010, Borrega et al., 2013a). Such important aspects of prehydrolysis as alteration of lignin (Klemola, 1968, Wayman and Lora, 1979, Lora and Wayman, 1980, Leschinsky et al., 2008a, Leschinsky et al., 2008b, Borrega et al., 2011b, Rauhala et al., 2011) and lignin-carbohydrate complex (Tunc et al., 2010, Westerberg et al., 2012) structures received detailed attention. With the notion of recovering the

released carbohydrates, the research focus was placed on detailed characterisation of hemicellulose products (Garrote et al., 1999b, Vázquez et al., 2005, Garrote et al., 2007, Nabarlatz et al., 2007) and handling techniques available for prehydrolysates (Gütsch and Sixta, 2011, Koivula et al., 2012).

The prehydrolysis process is accompanied mainly by acid-catalysed hydrolytic cleavage of the glycosidic bonds which results in solubilisation of hemicelluloses in the form of XOS. With increasing prehydrolysis intensity, dissolution is followed by further depolymerisation of XOS into monomers and degradation of the monomers in the solution primarily to furfural. When the process is carried out in pure aqueous conditions (autohydrolysis), the release of acetic acid from wood hemicelluloses facilitates hydrolysis (Rydholm, 1964, p. 665) .

Xylan dissolution in prehydrolysis follows pseudo-first order kinetics (Conner, 1984). A number of authors proposed that two fractions of xylan can be distinguished in wood: the first is represented by fast-reacting xylan while the other is comprised of more resistant xylan (Conner, 1984, Nabarlatz et al., 2004, Borrega et al., 2011a). Two parallel pseudo-first order reactions proceeding at different rates are therefore accounted for when deriving a kinetic expression for xylan degradation, as follows:

$$-\frac{dX}{dt} = z_X \cdot k_{f,X} \cdot X_f + (1 - z_X) \cdot k_{s,X} \cdot X_s \qquad (2.1),$$

where X is the fraction of wood xylan remaining in the solid residue, X_f and X_s are the fractions of the fast- and slow-reacting xylan in the residue, respectively, and z_X is the fraction of the fast-reacting xylan in wood (Sixta et al., 2006). Expression (2.1) can be integrated to yield

$$X = z_X \cdot Exp(k_{f,X} \cdot t) + (1 - z_X) \cdot Exp(k_{s,X} \cdot t) \qquad (2.2),$$

for calculating the dissolution of wood xylan.

The autohydrolysis intensity (P-factor) is a value combining treatment temperature and duration. Early attempts to develop a P-factor were made by Brasch and Free (1965), employing the idea that the autohydrolysis rate triples when temperature is increased by 10 °C. The relative rate, therefore, equalled 3((t-100)/10), where t represented temperature and 100 °C was selected as a unity related to at any given temperature. The P-factor was then determined as the area under the relative rate vs time curve. Later, an Arrhenius type equation was applied to express the relative rate (K_{rel}) as follows:

$$K_{rel} = \frac{k_{H,(T)}}{k_{H,100^\circ C}} = Exp\left(\frac{E_{A,H}}{R \cdot 373.15} - \frac{E_{A,H}}{R \cdot T}\right) \qquad (2.3),$$

where $k_{H,(T)}$ is the hydrolysis rate at temperature T, $k_{H,100°C}$ is the hydrolysis rate at 100 °C, $E_{A,H}$ is the activation energy and R is the gas constant (Sixta et al., 2006). The relative rate is integrated on a time interval to yield the P-factor:

$$P = \int_{t_0}^{t} \frac{k_{H,(T)}}{k_{H,100°C}} dt = \int_{t_0}^{t} Exp\left(\frac{E_{A,H}}{R \cdot 373.15} - \frac{E_{A,H}}{R \cdot T} \right) dt \qquad (2.4).$$

Autohydrolysis is a simple and economically viable pre-treatment technique, but it requires higher treatment intensities than acid prehydrolysis. Nevertheless, until recently, autohydrolysis in the aqueous phase had limited commercial applicability due to the formation of reactive lignin species that affect subsequent delignification and processing of the liquid prehydrolysates (Rydholm, 1964, Leschinsky et al., 2008a, Leschinsky et al., 2008b). In addition, wood prehydrolysates were not previously considered for the recovery of hemicelluloses and were burnt in the recovery boiler to produce energy. Steam prehydrolysis as a special case of autohydrolysis has been used as the primary technique to reduce hemicellulose content in wood prior to alkaline pulping. The process was developed in order to avoid the necessity of evaporating prehydrolysates before the recovery boiler. However, the replacement of water by steam resulted in poor delignification, bleachability and reactivity of resulting pulps. Eliminating the pressure release before the cooking stage and introducing immediate displacement neutralisation solved the limitations of steam prehydrolysis and resulted in the commercial Visbatch® pulping process (Sixta, 2006b).

In terms of combined hemicellulose recovery and pulp production, steam prehydrolysis is less appropriate than aqueous-phase prehydrolysis. Following the improvements in the technology of aqueous-phase prehydrolysis, its potential to replace steam pre-treatment has been recently commercially demonstrated in a continuous digester system (ANDRITZ, 2012, Råmark and Leavitt, 2012). Pilot-scale application of a flow-through autohydrolysis setup was also successfully demonstrated by Kilpeläinen et al. (2014).

The introduction of acids to catalyse prehydrolysis allows for lowering prehydrolysis intensities, thus reducing energy demand. Sulphuric acid is typically used for prehydrolysis (Springer, 1985, Rudie et al., 2007) while other mineral acids have not gained a commercial importance. The use of organic acids could be an interesting process alternative (Rudie et al., 2007, Gütsch et al., 2012). However, using acids for prehydrolysis has limited benefits due to high costs caused by limited recyclability and potential corrosion problems.

2.3.2 Post-hydrolysis

Borrega and Sixta (2013) reported on the possibilities of purifying paper-grade pulps by applying reinforced water post-hydrolysis to unbleached birch kraft pulp in a flow-

through system. Approximately 50-80% of the xylan contained in the pulp was extractable, essentially as XOS, with hot water. However, small amounts of cellooligosaccharides and up to 50% of pulp lignin were also dissolved. At the same time, the DP of the treated pulp decreased substantially with increasing xylan removal. Importantly, higher post-hydrolysis temperatures favoured better cellulose preservation at comparable residual xylan contents. Heikkilä et al. (2004) also reported a method to produce monomeric xylose by acid-catalysed post-hydrolysis of kraft pulps. The authors claimed that a minimum of 5% xylose on oven dry (o.d.) pulp can be obtained while maintaining the pulp viscosity at an acceptable level of 300 mL/g.

Potential replacement of prehydrolysis by a post-hydrolysis stage may result in a reduced yield of isolated xylan due to the loss of easily extractable xylan during the alkaline pulping stage. On the other hand, in aqueous post-hydrolysis, degradation of the isolated XOS can be reduced due to the absence of the acetic acid that is released from acetylated hemicelluloses during pre-hydrolysis. In addition, the absence of dissolved lignin facilitates the purification of the released XOS (Borrega and Sixta, 2013). Finally, the use of a flow-through system in both pre- and post-hydrolysis minimises the conversion of XOS to monomers and further degradation products (Kilpeläinen et al., 2012, Borrega and Sixta, 2013).

2.3.3 Alkaline and near-neutral pre-extraction

A number of research groups performed successful studies on alkaline pre-extraction of hardwoods (Al-Dajani and Tschirner, 2008, Al-Dajani and Tschirner, 2010, Schild et al., 2010, Walton et al., 2010, Yoon et al., 2011, Lehto and Alen, 2013, Vena et al., 2013) and annual plants (De Lopez et al., 1996, Fang et al., 1999, Puls et al., 2005) before pulping. The solubility of hemicelluloses in aqueous solutions of alkali is stipulated by partial ionisation of the macromolecules leading to better hydration, swelling and solvation (Dudkin et al., 1991). Alkaline pre-extraction can be performed under mild temperature conditions with a minimal impact on cellulose and lignin structure (De Lopez et al., 1996, Al-Dajani and Tschirner, 2008, Al-Dajani and Tschirner, 2010).

In near-neutral pre-extraction conditions, alkali is largely consumed for the neutralisation of the released acids, which results in pre-extracts in the near-neutral range of pH (Yoon et al., 2011, Lehto and Alen, 2013). When low alkalinity is applied, higher treatment intensities (temperature of 120-150 °C and retention time greater than an hour) are typically required to achieve wood yield loss similar to strongly-alkaline extractions. In the temperature range noted above, the contribution of carbohydrate degradation reactions is high (Lehto and Alen, 2013). The extracts obtained in near-neutral conditions are enriched with the degradation products, mainly organic acids, while the resulting content of the extracted xylan is rather low (Yoon et al., 2011, Lehto and Alen, 2013).

Applying pulping liquors (white and green kraft liquor, and soda-anthraquinone liquor) instead of pure alkali lowers the selectivity towards xylan extraction due to the presence of nucleophiles (hydrosulphide ions, AQ) (Sixta et al., 2006, Yoon et al., 2011).

It was demonstrated by Al-Dajani and Tschirner (2008) and Helmerius et al. (2010) that extracting 4-5% of xylan of o.d. wood at moderate to high temperatures and high alkalinity did not affect the yield of the subsequently produced kraft pulp, compared to a reference cook. A number of authors observed that the papermaking properties of the obtained pulps were comparable to those of the reference pulps after both alkaline (Al-Dajani and Tschirner, 2008, Al-Dajani and Tschirner, 2010, Schild et al., 2010) and near-neutral (Yoon et al., 2011) extractions. Importantly, the xylan extracted at high alkalinity had a molar mass greater than 21 kDa (Al-Dajani and Tschirner, 2008) indicating only minor degradation in the alkaline environment.

Despite the notable advantages of low-temperature high-alkaline extractions for the isolation of xylans without major degradation, there are a number of challenges associated with the process. First, efficient separation and purification methods should be developed. The techniques might include membrane filtration, precipitation, washing and dialysis. Second, the process requires efficient recycling of the non-consumed sodium hydroxide. Finally, energy balance has to be carefully considered to allow for a low temperature in the extraction stage.

2.3.4 Alkaline post-extraction

Alkaline post-extraction of hemicelluloses is traditionally used to remove residual hemicelluloses and optimise molar mass distribution of the dissolving pulps. Hamilton and Quimby (1957) showed that NaOH, KOH and LiOH all have similar potential for extracting xylan. Hot and cold caustic extractions are the two different techniques applied, depending on the desired results and the pulp type. Cold caustic extraction (CCE) is carried out at low temperatures of 20-40°C and high alkali concentrations of 5-12% (Fengel and Wegener, 1984) and is a physical dissolution process without a major chemical modification of xylan. Hot caustic extraction (HCE), which is only useful for sulphite pulps, is carried out at elevated temperatures of 70-130°C and low alkali concentration below 2%. Under HCE conditions, alkaline peeling reactions of the polysaccharide REGs are responsible for the removal of hemicelluloses. The same reactions, however, also cause significant cellulose yield loss. CCE is more selective towards isolation of xylan and is accompanied by smaller cellulose losses and xylan degradation than HCE. The selection of optimal CCE conditions is governed by the wood species and the degree of purity before the CCE stage. In general terms, higher alkali concentration and lower temperatures, which enhance the degree of cellulose swelling, improve the extraction efficiency (Sixta, 2006b). On the other hand, as a result of high alkali concentration, a gradual transformation of cellulose I to Na-cellulose I occurs,

which, upon washing, results in the formation of a cellulose II structure. The transformation behaviour of a pulp as a function of NaOH concentration depends strongly on the pulping method and on the raw material. For acid sulphite dissolving wood pulps, the transformation begins at NaOH concentrations of 6-7%, while a concentration of 10% is required for cotton linter pulps. The transformation of both substrates is completed at concentrations of 14-15%. (Wallis and Wearne, 1990, Sixta, 2006a) After this transformation, cellulose is less crystalline and more accessible to reagents (Sears et al., 1982). However, the reactivity of cellulose II towards derivatisation decreases upon thermal drying, due to formation of the inter- and intra-planar hydrogen bonds (hornification) (Sears et al., 1982, Oksanen et al., 1997).

The placement of the CCE stage in the bleaching sequence does not affect the degree of pulp purification (Sixta, 2006b). CCE is carried out either after washing before entering the bleach plant, after oxygen delignification or after the final bleaching stage. The obtained extract solution, depending on the stage placement, might be contaminated with small amounts of residual lignin and other degradation products. Svenson and Li (2005) developed a process for manufacturing pure xylan from partially bleached pulp by cold caustic extraction. The xylan was isolated from the retentate of the nanofiltrated CCE-extract. The possibility of producing food-grade xylose or xylitol was reported by the authors. Fuhrmann and Krogerus (2009) and Alekhina et al. (2014) reported that pure polymeric xylan was successfully extracted and separated by precipitation from commercial bleached paper grade pulps. The suggested applications of the polymer included strength and surface enhancing additives in papermaking (Fuhrmann and Krogerus, 2009) and a raw material for manufacturing oxygen barrier films after chemical modification (Alekhina et al., 2014).

2.3.5 Post-extraction with ionic liquids

Ionic liquid (IL) is a salt comprised of an organic cation and an inorganic or organic anion which is liquid below 100°C. Some ILs including those based on imidazolium cations are capable of dissolving cellulose and hemicelluloses (Brandt et al., 2013). Froschauer et al. (2013) observed that the addition of a certain amount of water to a cellulose solvent 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]) reduced cellulose dissolving capacity to basically zero, while rendering the IL highly selective towards hemicellulose extraction. Extraction of xylan from hardwood pulp (IONCELL-P process) was performed at 60 °C for 3h and resulted in the separation of xylan at a high yield into the liquid phase. After filtration, polymeric xylan could be isolated by water precipitation from the filtrate. Roselli et al. (2014a) demonstrated that 1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM][DMP]) had enhanced efficiency and selectivity towards xylan extraction from hardwood pulps compared to [EMIM][OAc]. In that process, 95% of xylan was extracted from birch pulp with only about 1 % of cellulose dissolved simultaneously. When applied to a bleached pine kraft pulp, both ILs efficiently extracted

xylan, while [EMIM][OAc] favoured the extraction of GGM and cellulose retention. However, extraction of GGM (residual content of 2.2% bleached pulp / initial content 7.1% bleached pulp) appeared to be more challenging than that of xylan (residual content 0.9% / initial content 8.1% bleached pulp) (Roselli et al., 2014a). IL extraction of xylan is not accompanied by yield losses or degradation of either the xylan or cellulose fraction. Furthermore, unlike in alkaline extraction, cellulose I crystalline form is completely retained. It was also demonstrated that by applying IL extraction, paper pulps could be upgraded to high-purity acetate grade pulps (Sixta et al., 2013, Roselli et al., 2014b). IONCELL-P extraction of birch paper pulp with a binary ionic liquid-water system was also studied by applying other ionic liquids (1-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethylphosphate, 1,5-diazabicyclo[4.3.0]non-5-enium acetate, 1,5-diazabicyclo[4.3.0]non-5-enium propionate) and N-methyl-morpholine N-oxide (Roselli et al., 2013). All systems were capable of dissolving xylan with varied efficiency and selectivity. IL-based hemicellulose isolation processes are still at the beginning of their potential for development.

2.3.6 Nitren post-extraction

Nitren is a metal complex of tris(2-amino-ethyl)amine and nickel (II) hydroxide in 1:1 proportion with a pH of 13. The complex is capable of dissolving cellulose. In aqueous solutions in the concentration range of 3-7 wt%, nitren is selective towards extracting xylan from pulps. In the presence of nitren solutions hydrogen bonds are first broken through deprotonation of the hydroxyl groups at C2 and C3 positions. Subsequently, the diolate moieties are bound to the central nickel atom via cis-configured hydroxyl groups in nitren by strong coordinate bonding (Janzon et al., 2006).

Puls et al. (2006) and Janzon et al. (2006) demonstrated that for xylan extraction, nitren is a more efficient reagent than sodium hydroxide at notably lower concentrations. Puls et al. (2005), Puls et al. (2006) and Janzon et al. (2008a) confirmed the possibility of extracting up to 98% of xylan in birch and eucalyptus pulps in polymeric form. Nitren solutions at concentrations of lower than 5% exhibited very high selectivity towards xylan with less than 2% of co-extracted cellulose. However, when the nitren concentration was increased to 7%, cellulose yield and extracted xylan purity were compromised due to the co-extraction of cellulose. Puls et al. (2005) reported that at a nitren concentration of 6% and treatment duration of 1 h at 30 °C an optimum pulp purity of birch kraft pulp of 4.7% extracted pulp (3.5% initial pulp with the extraction yield of 75%) was achieved at a cellulose yield loss of 3.6% initial pulp. Janzon et al. (2008a) and Puls et al. (2006) also observed that at similar yields and purities, xylan of higher molar masses were precipitated from their solutions after nitren extraction as compared with 10% NaOH and 14% KOH extractions. The obtained nitren-extracted xylan met the required specifications for the alkali-extracted polymeric xylan.

Nitren extraction is suitable for both kraft and sulphite pulps. The process is limited to isolating xylan and is inefficient for glucomannan extraction. Similarly to IL-extracted pulps, nitren-extracted pulps retain a cellulose I structure (Janzon et al., 2008b). The major concern of nitren extraction is the presence of nickel, which has to be carefully removed from the extracted xylan and pulps.

2.3.7 Enzymatic treatment

Enzymatic treatments are an important tool to convert isolated xylan or its depolymerisation products into chemicals, fuels and food. Besides, enzymatic hydrolysis can be used as an aid to chemical isolation of xylan or even as a standalone process. Specific enzyme groups applicable to hardwood xylan deconstruction are (1) endo-β-1,4-xylanase, (2) exo-1,4-β-xylosidase, (3) α-glucuronidase and (4) acetyl xylan esterase (Shallom and Shoham, 2003). Group (1) enzymes hydrolyse the backbone of polymeric β-1,4-xylan into short XOS. Group (2) uses β-1,4-xylooligomers and xylobiose as a substrate to produce xylose by stepwise hydrolysis of end-xylopyranose units. Group (3) functions by cleaving glucuronic acid substituents from the 4-*O*-methyl-α-glucuronic acid (1→2) xylooligomers. Group (4) can hydrolyze the acetyl substituents on xylose moieties of 2- or 3-*O*-acetyl xylan (Shallom and Shoham, 2003). Since lignin is known to have an inhibitory effect on enzymes (Rahikainen et al., 2013), enzymatic hydrolysis can be performed only in essentially lignin-free systems (Dudkin et al., 1991).

Hakala et al. (2013) studied isolation of xylan by enzyme-aided alkaline extraction. The authors reported that a mixture of polymeric xylan and XOS could be extracted from pulps previously treated with xylanase or endoglucanase. A two-stage alkaline extraction with an enzymatic treatment between the stages allowed maximising total extraction efficiency.

Enzymatic hydrolysis of hemicelluloses in pulp has been extensively studied as means of cellulose purification (Puls et al., 1987, Christov and Prior, 1993, Köpcke et al., 2008, Ibarra et al., 2010, Gehmayr et al., 2011, Gehmayr and Sixta, 2012). When endo-β-1,4-xylanase was applied to bleached high xylan-content kraft hardwood pulps, the maximum removal of xylan already occurred at small xylanase dosages (Puls et al., 1987). However, significant amounts of xylan remained in the pulp after the treatments (Köpcke et al., 2008, Ibarra et al., 2010). Sequential pulp enzymatic and chemical treatments can be applied successfully to pulps with high hemicellulose content. Köpcke et al. (2008) and Gehmayr et al. (2011) investigated upgrading possibilities for bleached and oxygen delignified birch paper-grade kraft pulps to dissolving pulps by introducing a xylanase treatment stage before alkaline post-extraction. In the xylanase treatment stage, 46% of pulp xylan was solubilised. As a result, the caustic concentration in the alkaline stage could be reduced, minimising the formation of Na-cellulose I complex while maintaining xylan extraction at the target level.

Fairly poor performance of xylanases on bleached pulps was discussed by Christov and Prior (1993), Suurnäkki et al. (1996) and Gübitz et al. (1997). They suggest that the xylan easily accessible to enzymes is removed from pulps during bleaching while the remaining fraction undergoes modification resulting in its low accessibility. Additionally, the size of the enzyme may prevent interaction with poorly accessible hemicelluloses. Gubitz et al. (1998) also reported that approximately half of the hemicelluloses in a bleached softwood pulp that were resistant to enzymatic hydrolysis was associated with lignin-hemicellulose complexes. The presence of both glucomannan-lignin and xylan-lignin complexes is believed to limit hemicelluloses removal by enzymatic treatment.

2.3.8 Spent pulping liquors as a source of carbohydrates

Spent pulping liquors may serve as a source of hemicelluloses. In sulphite pulping, acid-catalysed hydrolysis of hemicelluloses enriches spent liquors with carbohydrates accessible for further processing. Spent sulphite liquors may contain dissolved hemicelluloses of 13 and 10% o.d. wood as reported for beech and spruce dissolving pulps, respectively (Sixta et al., 2006). The composition of the spent sulphite liquors depends largely on the wood species and pulping conditions. Carbohydrates in monomeric form dominate in acid sulphite spent liquors (Sixta et al., 2006). The spent liquors are upgraded to allow conversion of the dissolved carbohydrates into end products. Additionally, hemicellulose degradation products – furfural (1% and 0.2% o.d. wood for beech and spruce, respectively) and acetic acid (6.2% and 2.7% o.d. wood for beech and spruce, respectively) – are separated from the spent liquors at the evaporation stage with subsequent liquid-liquid extraction and distillation (the values are reported for the dissolving pulp spent liquors) (Sixta et al., 2006).

In the kraft pulping process, about half of wood hemicelluloses are dissolved. However, in the spent liquors, dissolved carbohydrates are substantially degraded to aliphatic hydroxycarboxylic acids. For that reason, the abundance of carbohydrates in the softwood and hardwood spent liquors typically does not exceed 1-1.5% and 3-4% o.d. wood, respectively. (Alen, 2000b) Furthermore, in black liquor, lignin and its degradation products are present in the amounts notably exceeding those of carbohydrates (Wallberg et al., 2006) which makes isolation of the pure carbohydrates very challenging. However, isolation of the carbohydrates is seen as a potential route to utilise black liquor (Wallberg et al., 2006, Niemelä et al., 2008). Niemelä et al. (2008) demonstrated that pulping conditions strongly affect the percentage of carbohydrates in black liquor, which could be important when hardwood black liquors are considered as a source of hemicelluloses. Paananen et al. (2013) reported that high alkalinity favoured retention of both xylan and galactoglucomannan in softwood spent liquors. Wallberg et al. (2006) isolated lignin and hemicelluloses from black liquor by membrane filtration. It was reported that the highest retention was observed for glucan, xylan, and arabinan.

2.4 Chemical aspects of xylan isolation

2.4.1 Wood degradation in acidic environment

Prehydrolysis alters all wood components due to the lack of selectivity towards hemicellulose dissolution (Figure 2.6). The extent of such alteration is strongly dependent on the process severity and may impose undesired properties to both the wood residue and the hydrolysate.

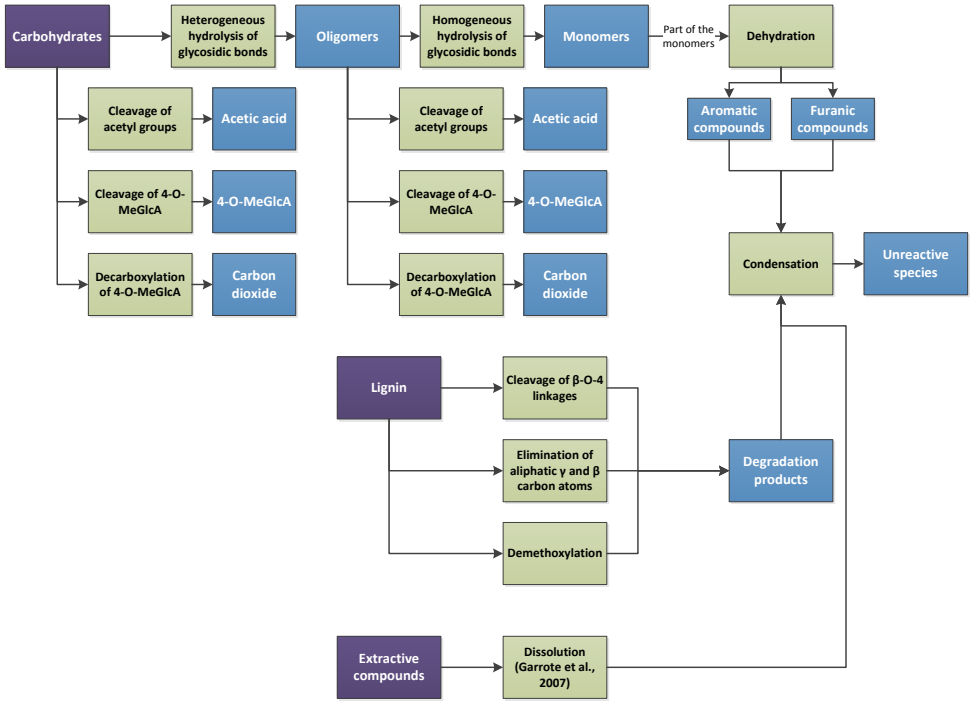

Figure 2.6. Simplified scheme of the reactions occurring during prehydrolysis with the wood components.

Depolymerisation through hydrolytic cleavage of the glycosidic bonds is one of the major reactions of polysaccharides occurring in the entire pH range from acidic to alkaline (Bobleter, 2004). In acidic environments, gradual hydrolysis to monomers is followed by further conversion to degradation products (Figures 2.7 and 2.8). Hemicelluloses undergo a number of hydrolytic reactions in aqueous and acid-catalysed prehydrolysis (Nabarlatz et al., 2007, Gullon et al., 2010, Li et al., 2010, Borrega et al., 2011a). First, cleavage of acetyl substituents from the acetylated polysaccharides starts and continues throughout prehydrolysis. In autohydrolysis, such cleavage creates an acidic environment to catalyse the hydrolytic reactions. Heterogeneous hydrolysis of glycosidic bonds in the solid phase proceeds at two different rates: the fast initial and the slow

secondary stage, owing to restricted accessibility of hemicelluloses (Leschinsky et al., 2009, Testova et al., 2009). The bonds between the xylose moieties and the uronic acid substituents are essentially more resistant to acid hydrolysis, which proceeds at much lower rate (Dudkin et al., 1991). In addition to the cleavage of glucuronic acid substituents, decarboxylation reactions proceed in acidic environment. The reaction in strong acidic conditions has been used to determine quantitatively the content of uronic acids in polysaccharides (Nanji et al., 1925). The reaction is also believed to occur in mild prehydrolysis conditions resulting in the discrepancies in the mass balance of the uronic acid after prehydrolysis. Leschinsky et al. (2009) suggested that CO_2 released in prehydrolysis originated from such decarboxylation reactions. Deacetylation, depolymerisation and degradation of the dissolved hemicelluloses continue in the liquid phase. Liquid hydrolysates typically contain free acetic acid, hemicelluloses in polymeric, oligomeric and monomeric form, and degradation products such as furfural and hydroxymethyl furfural (HMF). Additionally, a number of degradation products (primarily aliphatic carboxylic acids) can be found in wood prehydrolysates (Borrega et al., 2013b). Formic acid, one of the most abundant degradation products (Borrega et al., 2013b), is believed to be formed through acid-catalysed rehydration of furanic compounds (Williams and Dunlop, 1948, Salak Asghari and Yoshida, 2006). Furanic compounds easily undergo condensation reactions with other furanic compounds or with fragmented lignin (Figure 2.8). It has also been reported that under acidic conditions other aromatic compounds are formed from carbohydrates as a result of dehydration, degradation, and recondensation (Sixta et al., 2006). The reaction proceeds through the elimination of a water molecule from two hydroxyl groups to form levoglucosan. The resulting aromatic compounds include primarily benzenediole, benzofuran, benzopyran and benzoic acid structures (Sixta et al., 2006, p.420).

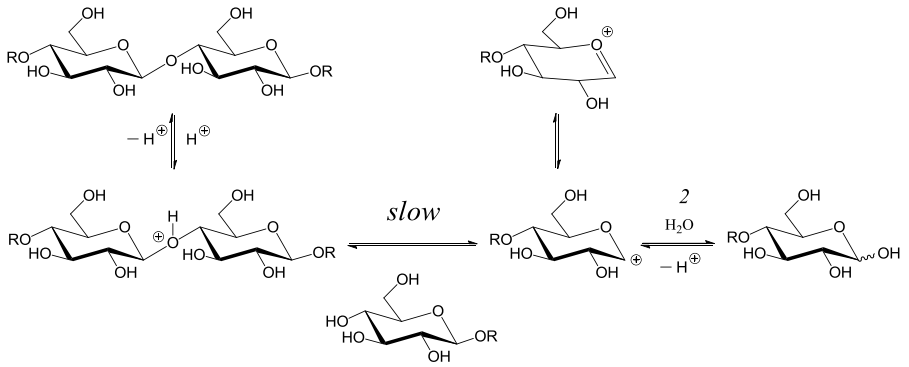

Figure 2.7. Acid hydrolysis of polysaccharides (adopted from Sixta et al. 2006, p. 416).

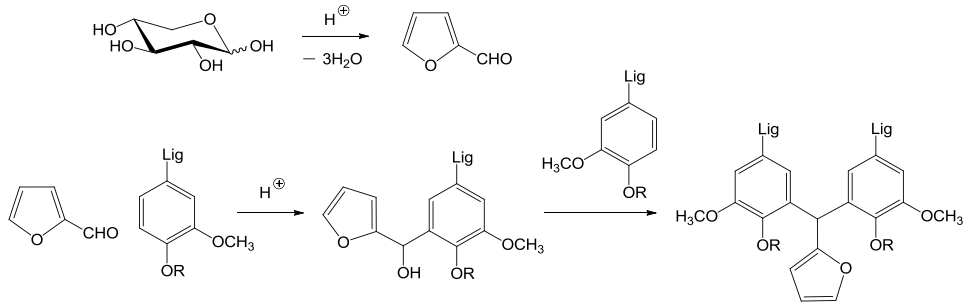

Figure 2.8. Degradation of pentoses under acidic conditions and condensation of the formed furfural with lignin units (adopted from Sixta et al. 2006, p. 420).

Cellulose is more resistant to hydrolysis than hemicelluloses owing to its highly ordered structure. Furthermore, in autohydrolysis, acetic acid with a low dissociation constant provides only limited hydrolysis of glucans (Bobleter, 2004). In mild prehydrolysis conditions, accessible fractions of cellulose undergo random hydrolytic cleavage leading to reduced DP but not affecting cellulose yield (Tunc and van Heiningen, 2008). However, at higher intensities, substantial cellulose yield loss associated with a severe hydrolytic attack is observed (Borrega et al., 2011a).

Lignin behaviour under prehydrolysis conditions is complex. Homolytic cleavage of the β-O-4 linkages proceeds only in the presence of a free phenolic hydroxyl group and results in depolymerisation of lignin (Meshgini and Sarkanen Kyosti, 1989, Bobleter, 1994, Li et al., 2000, Fasching et al., 2006). The resulting formation of the new phenolic hydroxyl groups triggers continuous cleavage reactions of the β-O-4 linkages in prehydrolysis conditions (Sarkanen and Ludwig, 1971, Fasching et al., 2006). At the same time, the content of the aliphatic hydroxyl groups is reduced due to the elimination of aliphatic γ- and β- carbon atoms (Klemola, 1968). Demethoxylation of hardwood lignin also occurs in prehydrolysis to a small extent resulting in decreased syringyl-to-guaiacyl ratio (Rauhala et al., 2011). Some lignin fragments dissolve into the hydrolysate while the species remaining in the solid phase may be extracted by organic solvents (Lora and Wayman, 1978a). Formation of reactive lignin structures is followed by recondensation decreasing lignin reactivity (Leschinsky et al., 2008a, Leschinsky et al., 2008b). The amount of the residual lignin in the solid phase decreases as a function of prehydrolysis intensity until a certain intensity is reached. At high prehydrolysis intensities, condensation reactions start to dominate rendering lignin insoluble (Borrega et al., 2011b). The dissolved reactive phenolic species initiate the generation of sticky precipitates which cause difficulties in further processing of the hydrolysates. Measures to overcome such difficulties have been studied (Gütsch and Sixta, 2011, Koivula et al., 2012). Gütsch and Sixta (2011) demonstrated the possibility of efficiently removing lignin degradation products from the hydrolysates by applying activated charcoal treatment at the prehydrolysis temperature.

2.4.2 Wood degradation in alkaline environment

Carbohydrates undergo a number of reactions in alkaline environments (Figure 2.9). Acetylated hemicelluloses are subjected to fast near-quantitative deacetylation by saponification of ester bonds. Cleavage of the terminal reducing anhydrosugar units through β-elimination reaction is called alkaline peeling (Figure 2.10) (Klemm et al., 1998) (Ea = 102.9 kJ/mol for cellulose (Haas et al., 1967), 113 kJ/mol for softwood galactoglucomannan (Paananen et al., 2010)). This reaction results in the formation of free isosaccharinic acids and new REGs (Figure 2.11). Peeling reaction is already initiated at low temperatures (about 80 °C) and continues in a stepwise fashion until the equilibrium conditions of the keto-enol tautomerization are favourable for 1,2-enolate formation, which is the prerequisite for the chemical stopping reaction (Figure 2.12). There, the REG is converted to metasaccharinic acid (MSA), which is stable against alkaline peeling (Ea stopping = 134.7 kJ/mol for cellulose (Haas et al., 1967) 113 kJ/mol for softwood galactoglucomannan (Paananen et al., 2010)). The ratio between the peeling and stopping reaction rate constants is dependent on the alkali concentration (Paananen et al., 2010). In addition, peeling reaction may be also terminated by physical stopping due to restricted accessibility when approaching crystalline domains. Termination of peeling reaction is also achievable by oxidation or reduction of the REG into aldonic acid or alditol, respectively.

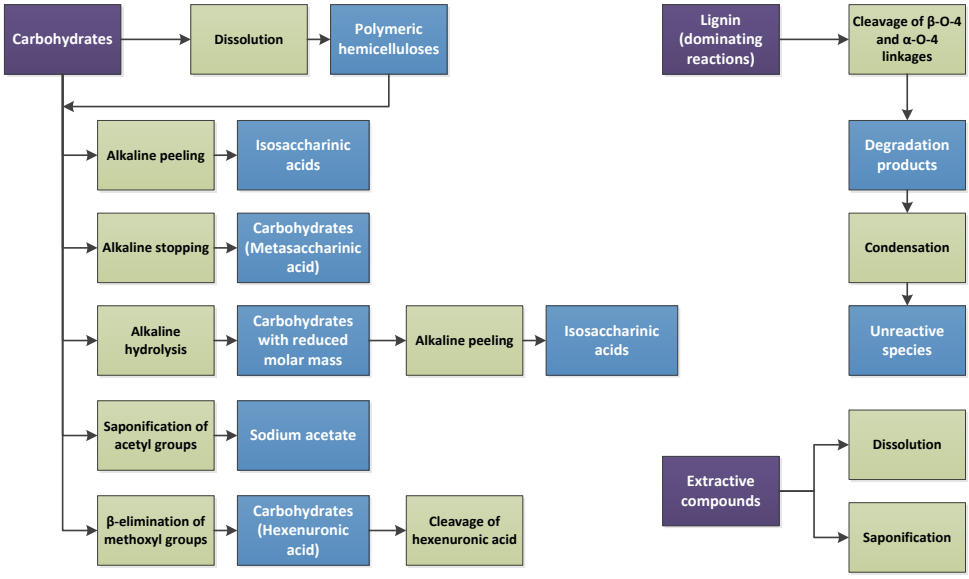

Figure 2.9. Simplified scheme of the reactions occurring during alkaline pre-extraction with the wood components.

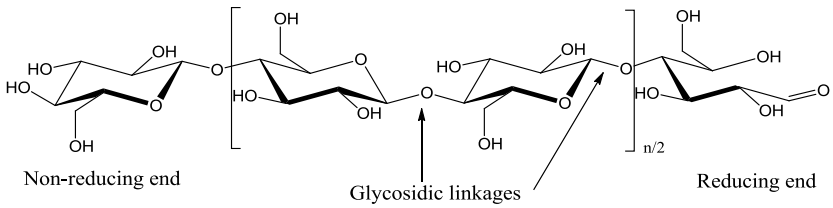

Figure 2.10. Carbohydrates undergo alkaline degradation at the reducing end and at the glycosidic linkages as illustrated in the cellulose molecule.

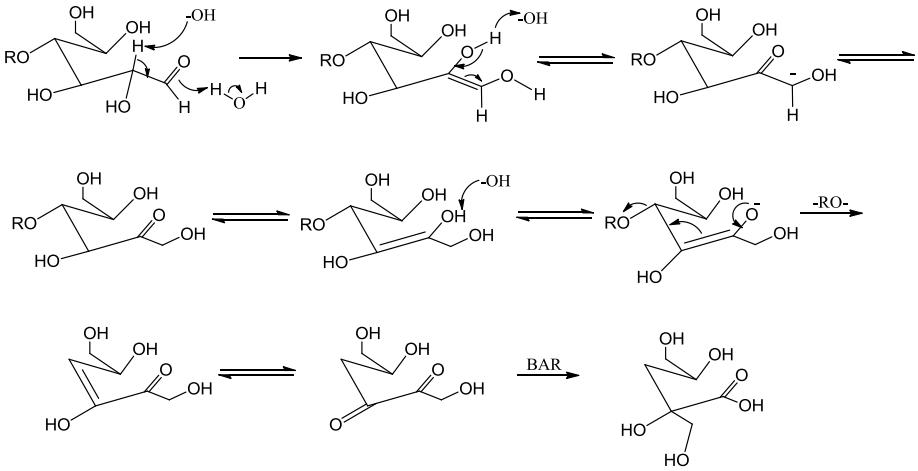

Figure 2.11. Mechanism of alkaline peeling shown for cellulose. BAR –benzilic acid rearrangement, R – cellulose chain (adopted from Sixta et al. 2006, p. 176).

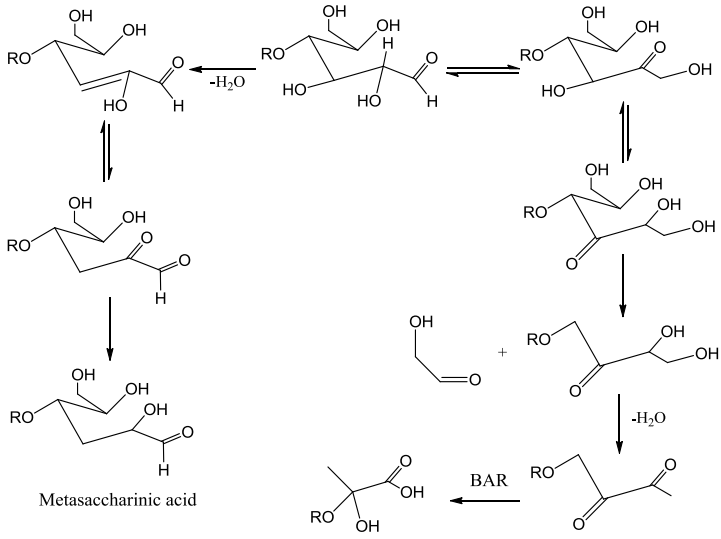

Figure 2.12. Mechanism of chemical stopping shown for cellulose. BAR – benzilic acid rearrangement, R – cellulose chain (adopted from Sixta et al. 2006, p. 176).

Secondary peeling occurs at the newly generated REGs due to alkaline hydrolysis (Ea = 150.2 kJ/mol for cellulose) involving random cleavage of glycosidic bonds (Figure 2.13) (Lai and Sarkanen, 1967). Alkaline hydrolysis is more significant at higher temperatures than peeling and stopping reactions (>140 °C). Alkaline hydrolysis strongly affects the DP of a polysaccharide whereas the peeling reaction is responsible for the yield loss.

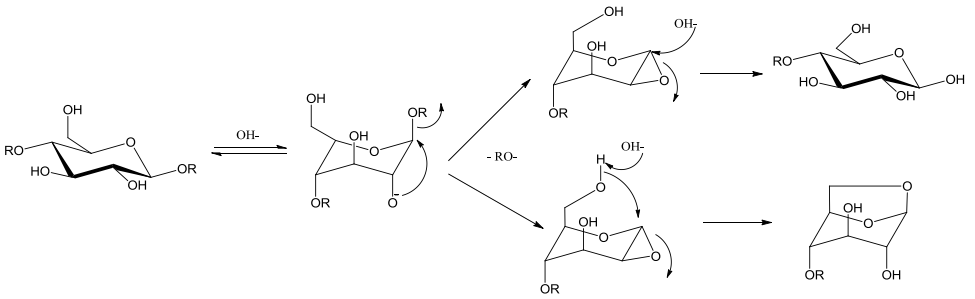

Figure 2.13. Mechanism of alkaline hydrolysis shown for cellulose. R – cellulose chain (adopted from Sixta et al. 2006, p. 178).

Wood polysaccharides undergo peeling reactions at different rates. The mannose end unit in glucomannans is more stable to isomerisation than the anhydroglucose unit in cellulose; however, due to its entirely amorphous structure the extent of glucomannan degradation is more substantial than that of cellulose. Linear xylans, on the other hand, are the most susceptible to peeling reactions, whereas the 1→2 linked substituents like glucuronic acid and rhamnose residues slow down the reaction (Figure 2.14) and 1→3 linked arabinose residue in softwood xylans leads to stabilisation of the REGs through β-elimination of the arabinose residue and formation of a terminal MSA unit (Dudkin et al., 1991). MeGlcA substituents are gradually converted to hexenuronic acid substituents through β-elimination of methoxyl groups in alkaline conditions (Teleman et al., 1995) which can be either partly or completely eliminated in alkali and acid, respectively (Figure 2.15). Degradation of carbohydrates results in notable alkali consumption due to the formation of free acids (Dudkin et al., 1991).

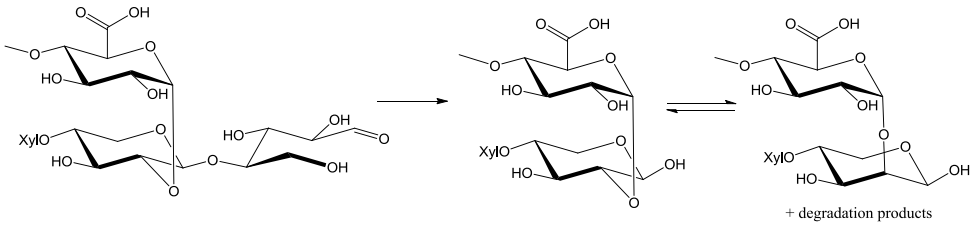

Figure 2.14. Stopping of xylan peeling at the 1→2 linked glucuronic acid substituent. Xyl – xylan chain (adopted from Sixta et al. 2006, p. 179).

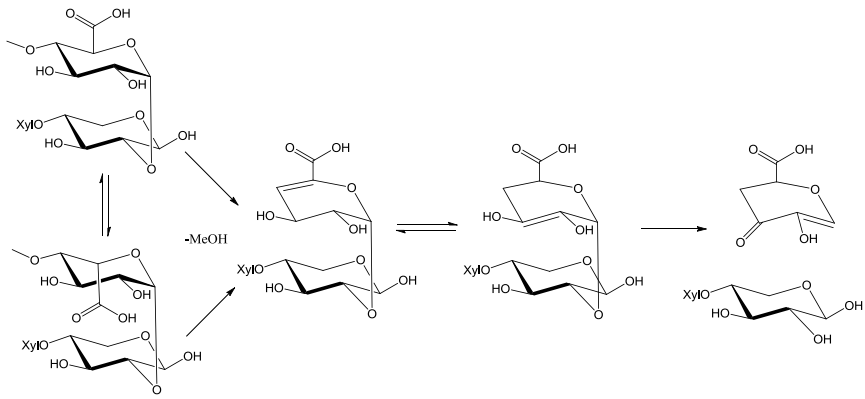

Figure 2.15. Mechanism of formation of hexenuronic acid by demethylation of glucuronic acid and elimination of the hexenuronic acid unit in alkaline conditions. Xyl – xylan chain (adopted from Sixta et al. 2006, p. 180).

Alkali is a weak nucleophile initiating lignin depolymerisation and dissolution through the cleavage of alkyl-O-aryl, alkyl-O-alkyl and alkyl-O-carbohydrate ether linkages. The most common reactions in the presence of alkali at elevated temperatures (>100 °C) are cleavage of α-O-4 and β-O-4 linkages. The cleavage of β-O-4 linkages in non-phenolic structures proceeds in the presence of a free hydroxyl group at the α- or γ- position. In the absence of a strong nucleophile, phenolic β-O-4 structures typically undergo formation of quinone methide structures followed by the elimination of formaldehyde from the γ-carbon. The resulting vinyl ether structures may undergo condensation reactions with the released formaldehyde (Nikitin et al., 1978, Sixta et al., 2006). The linkage in the α-position can be cleaved by nucleophilic substitution only in the phenolic lignin structures. Free phenolic hydroxyls in lignin react with alkali to form phenolates. In general, in the presence of only a weak OH^--nucleophile, depolymerisation of lignin is followed by condensation (formation of C-C(Ar) linkages) particularly in guaiacyl structures in softwoods.

2.5 Effects of pre-treatments on alkaline pulping

Changes in the chemical composition and physical properties of wood upon pre-treatments in acidic and alkaline conditions affect wood behaviour in pulping. First, removal of the hemicelluloses opens up the wood's porous structure (Penttilä et al., 2013, Vena et al., 2013) which in turn leads to a better accessibility to cooking chemicals. As a result, the time required for the impregnation with cooking chemicals can be substantially reduced. Removal of wood constituents in the pre-treatment stage may also allow for tighter chip packing in the pulping stage and hence higher wood intake (van Heiningen, 2006, Huang et al., 2010).

Delignification efficiency in the pulping and oxygen stages increases as a function of prehydrolysis intensity when mild prehydrolysis is applied. This behaviour can be attributed to lignin depolymerisation and breakage of lignin-carbohydrate complexes (Schild et al., 1996, Rauhala et al., 2011). In this case, the pulping and oxygen stage can be carried out in milder conditions to achieve the same delignification (Sixta et al., 2006). Under more intense prehydrolysis conditions, reactive phenolic lignin species tend to form insoluble fractions (Sixta et al., 2006). This may not only result in pulps with increased kappa numbers but render pulps resistant to subsequent bleaching operations (Borrega et al., 2013a).

The removal of xylan during prehydrolysis reduces the content of MeGlcA substituents available for the formation of hexenuronic acids during pulping. The minimised formation of hexenuronic acid results in reduced consumption of oxidative chemicals in the bleaching sequence.

Prehydrolysis may negatively affect the retention of cellulose in the pulp due to the formation of new REGs (Sixta et al., 2013). The yield loss may be mitigated at the pulping stage by forced stabilisation of the reducing ends with oxidative, reductive or derivatising compounds (Clayton and Marraccini, 1966, Nilsson and Östberg, 1968, Lindenfors, 1980, Lehtaru and Ilomets, 1996, Copur and Tozluoglu, 2008).

Prehydrolysis may affect the properties of the resulting pulps. Pulps produced under mild prehydrolysis conditions may have higher viscosity than a reference due to the removal of short chain hemicelluloses (Testova, 2006). Prehydrolysis pulps typically exhibit inferior papermaking properties compared to the conventional alkaline pulps (Testova, 2006, Yoon et al., 2011).

Alkaline pre-extraction in mild conditions is rather selective towards the extraction of polymeric xylan, and is accompanied by only minor structural changes in wood components (Vena et al., 2013). In alkaline pre-extraction, the formation of hydroxyacids by peeling reactions is considerably reduced due to the enhanced removal of xylan by dissolution, which leaves more alkali available for delignification in the pulping stage. Therefore, lower pulping intensities or decreased alkali charges may be applied to achieve similar pulping results (Roselli, 2011). It has also been reported by a number of authors that papermaking properties of pre-extracted pulps can be maintained on the same level as the reference wood pulps (Al-Dajani and Tschirner, 2008, Schild et al., 2010, Yoon et al., 2011).

2.6 Some environmental and health aspects

Forest-based industry uses renewable feedstock to produce materials, chemicals and energy. A key to the future of biorefineries is continued development of sustainable

forestry, expanding processes to a wider range of feedstock including residues, use of greener techniques and more efficient separation processes (Clark et al., 2012).

Process industry impacts the environment by generating air emissions, effluents, solid wastes, and noise and heat (Dahl et al., 2008, Süss, 2008). Today, industries are committed to using resources in an optimal way and to minimising environmental impacts while maintaining high product quality. Pulp and paper has been a good example of fulfilling such commitments. Both fresh water use and the amount of released emissions and effluents have been regularly reduced through efficient purification systems and regeneration of chemicals (Dahl et al., 2008). In the future, more selective fractionation of biomass into individual components and subsequent conversion to end-use products should reduce the amount of organic waste and emissions. At the same time, use of safer chemicals in all process steps could reduce the risk of hazardous emissions.

At the moment, the most common chemical pulping technique is the kraft process (Sixta et al., 2006). Kraft pulp production utilises sodium hydroxide and sodium sulphide as pulping chemicals. The presence of sodium sulphide leads to generation of malodorous gaseous emissions in the pulping stage and sulphur oxides in the chemical recovery cycle (Süss, 2008). In a modern kraft pulp mill, these emissions are carefully controlled. Nevertheless, in order to avoid the risk connected with sulphur-containing emissions in a pulp mill, sodium sulphide may be replaced by another nucleophile, such as AQ. AQ, or 9,10-dioxoanthracene, is an aromatic organic compound with a general chemical formula $C_{14}H_8O_2$. The applicability of AQ to the pulping industry was discovered in the 1970s; it was discovered that adding small amounts of AQ to soda pulping liquor could enhance the delignification rate substantially (Fleming et al., 1978). Furthermore, different AQ derivatives have also demonstrated similar properties to greater or lesser extent (Evstigneev and Shalimova, 1985). Since then, AQ has been applied as a delignification and yield-increasing aid in a number of pulping applications (Blain, 1993, Francis et al., 2008). It was confirmed that SAQ process can produce pulp with properties similar to those resulting from the conventional kraft pulp process (Bose et al., 2009, Schild et al., 2010). Furthermore, sulphur-free spent liquor is favoured over kraft black liquor once the conventional recovery boiler is replaced by a more energy-efficient gasification process (Bose et al., 2009). The deficiencies of the SAQ process are lower pulp bleachability (Bose et al., 2009, Kanungo et al., 2009) and the need for increased recausticising capacity. Furthermore, AQ has recently been withdrawn from the list of recommended chemicals for the production of food packaging (BfR Federal Institute for Risk Assessment, 2013) due to its potential carcinogenic effect (International Agency for Research on Cancer, 2013). This latter development limits the applicability of the SAQ process to only certain product types.

3. Experimental

3.1 Materials

Industrially-acquired birch chips from UPM Pietarsaari (*Betula pendula*) were used for the experiments in Papers I, III and IV. The chips were screened and stored at -18 °C until shortly before the experiments. Cotton linters (CL) supplied by Milouban M.C.P. Ltd with an intrinsic viscosity of 950 mL/g was used as the model cellulose substrate in Paper II. The CL was ground before the experiments in a Wiley mill using a mesh size of 0.5 mm.

3.2 Equipment

Three reactors were used for pre-treatments, pulping and oxygen delignification (Table 3.1). The rotating air bath reactor with six stainless steel autoclaves of 2500 mL was used for the prehydrolysis experiments in Paper I, oxalic acid (OA) pre-treatment in Paper II and in Testova et al. (2012a), prehydrolysis at 170°C in Paper III, dissolving pulp production in Paper III and paper pulp production in Testova et al. (2012a). The same reactor was used to perform oxygen delignification in Papers III and IV, where the regular stainless steel autoclaves were replaced by the Teflon-coated equivalents. The rotating oil bath reactor with silicon oil as heat transfer medium and eight autoclaves of 220 mL each was used for the kinetic experiments in Paper II, for the alkaline pre-extraction optimisation in Paper IV and for the unpublished pulping experiments with sodium borohydride. A stationary jacketed 10-litre reactor with external liquid circulation was used for the high temperature prehydrolysis experiments in Paper III and the large scale alkaline pre-extraction and pulping in Paper IV. The small oil bath reactor was well suited to the optimisation experiments and to the model studies. The 10-litre reactor was used for the experiments where high temperatures and larger volumes of products were required. The use of the 10-litre reactor in Paper IV was motivated by the possibility of sequential pre-extraction and pulping without opening the reactor by means of liquor displacement, which most resembles industrial conditions. On the other hand, the advantage of the rotary reactors is more efficient mixing and, hence, improved mass transfer as well as a lower temperature gradient next to the reactor walls in the solid phase.

Figure 3.1. 10-litre reactor.

Figure 3.2. Air bath reactor autoclave.

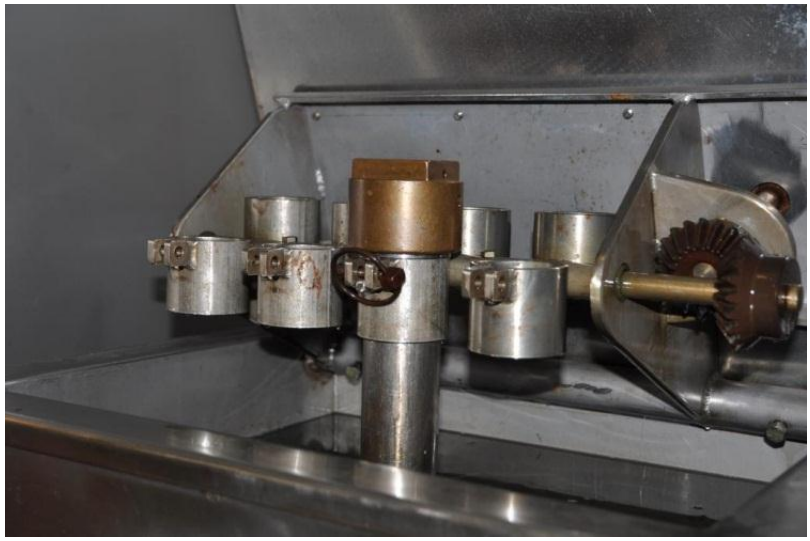

Figure 3.3. Oil bath reactor.

Table 3.1. Specification of the reactors.

	Air bath reactor	Oil bath reactor	Double-jacket 10 L reactor
Material	Stainless steel	Stainless steel	Stainless steel
Volume, L	6×2.5	8×0.22	10
Temperature limit, °C	200	200	250
Pressure limit, bar	20	<60	60
Technical concept	Rotary autoclaves in an air bath	Rotary autoclaves in an oil bath	Double-jacket, stationary
Liquid circulation	Autoclave rotation	Autoclave rotation	External circulation, Pump flow 10-30 L/h
Heating medium	Air	Silicon oil	Oil

3.3 Pre-treatments

3.3.1 Prehydrolysis (Papers I, II, III, and Testova et al. (2012a))

Aqueous-phase prehydrolysis or autohydrolysis of birch chips was performed at elevated temperatures from 150 to 220 °C at a liquid-to-solid ratio of 4 L/kg and varied duration times as described in Table 3.2. The combined time and temperature effect of prehydrolysis, known as the P-factor, was calculated using Arrhenius-type function (Eq. 2.4).

In Paper I, P-factor was calculated using the activation energy for fast-reacting xylan hydrolysis of 125.6 kJ/mol (Sixta et al., 2006). In Paper III, a modified P-factor expressed as log P_{Xs} with the activation energy of 180 kJ/mol, corresponding to the removal of the recalcitrant xylan fraction in birch wood (Borrega et al., 2011a) was used. The P-factor of 1000 in Paper I and the log P_{Xs} of 4.19 in Paper III corresponded to the same prehydrolysis conditions.

Oxalic acid prehydrolysis of wood in the study presented in Testova et al. (2012a) was performed under the conditions listed in Table 3.2.

OA prehydrolysis of CL in Paper II was performed at an acid concentration of 0.01 mol/L, 15 L/kg liquid-to-solid ratio, a treatment temperature of 110 ◦C, and an isothermal duration of 80 min. The selection of oxalic acid was governed by its medium acid strength (pKa1 = 1.27 and pKa2 = 4.28) and the absence of heteroelements. Wood prehydrolysis experiments in Testova et al. (2012a) were performed according to Table 3.2.

Table 3.2. Prehydrolysis conditions.

Denotation		P150	P170	P200	P220	P(OA)
Denotation in papers		P200	P1000, P170	P200	P220	P(OA)
Paper		I	I, III	III	III	Testova et al. (2012a)
Temperature	°C	150	170	200	220	120
Effective time	min	100	100	13.5	5	90
Liquid-to-solid ratio	L/kg	4	4	4	4	4
P-factor		200	1000	1198	1274	n.a.
Log Px_s		3.2	4.19	4.69	4.96	n.a.
Acid concentration	mol/L	n.a.	n.a.	n.a.	n.a.	0.05

n.a. – not applied

3.3.2 Alkaline pre-extraction (Paper IV)

Alkaline pre-extraction of wood was optimised by varying alkali concentration from 1 to 2.5 mol/L, temperature from 80 to 125 °C, and chip thickness (from 2-4 mm to 4-6 mm). The focus was placed on high alkalinity in the absence of a nucleophile with the goal of maintaining high selectivity towards xylan extraction. A high liquid-to-solid ratio of 9.3-10 L/kg was selected in order to avoid a substantial decrease in alkali concentration, which in turn could result in precipitation of xylan.

3.4 Pulp production (Papers III and IV)

All pulping experiments were performed by following the SAQ protocol with an effective alkali charge of 19-22% o.d. wood and an AQ charge of 0.075-0.1% o.d. wood (Table 3.3). Pulping of the alkali pre-extracted wood (E-SAQ) residue in optimal conditions (95°C, 2.5 mol/L NaOH) was performed after a pressure discharge of the liquid phase followed by an intermediate washing stage (liquid-to-solid ratio 1.2 L/kg) to remove the excess of alkali and recover an additional amount of extracted xylan (Paper IV). In the case of prehydrolysis, no intermediate washing of the wood residue was performed; the liquid phase was removed by pressure discharge (Paper III) or centrifugation (Testova et al. (2012a)).

Table 3.3. Pulping conditions.

Denotation		SAQ	E-SAQ	P(OA)-SAQ	P(OA)-SAQ-AQ	P(OA)-SAQ-AQS	P(OA)-SAQ-BH	P170	P170-BH	P200	P220
Pulp grade		Paper						Dissolving			
Included in		Paper IV		Testova et al. (2012a)				Paper III			
H-factor		800	550	400	350	450	750	350	300	200	200
AQ charge	% o.d. wood	0.1	0.075	0.1	0.1	0.1	0.1	0.1			
Effective alkali		20	19.1	20	20	20	20	22			
Stabilisation		n.a.	n.a.	n.a.	AQ	AQS	BH	n.a.	BH	n.a.	n.a
- charge	% o.d. wood	n.a.	n.a.	n.a.	0.75	0.7	1	n.a.	0.5	n.a.	n.a.

n.a. – not applied

Oxygen delignification of the pulps in Papers III and IV and bleaching in paper III was performed according to standard laboratory procedures.

3.5 Alkaline degradation (Paper II)

Alkaline degradation trials were carried out at a temperature of 160 ◦C, a liquid-to-solid ratio of 40 ml/g, and an alkali concentration of 20 g/L. Dispersed AQ was added to the alkaline solution at a concentration of 0.1 g/L except for the trials with AQS and selected trials with sodium borohydride (BH), where AQ was not applied, and the trials where AQ concentrations were varied to study its stabilisation effect. In the optimisation trials of stabilisation chemicals, fixed isothermal treatment duration (160 °C) of 64 min was applied. The kinetic study included alkaline degradation time series at 125 ◦C and 160 ◦C with durations of up to 70 h and 5 h, respectively.

3.6 Stabilisation

Stabilisation of cellulose fraction against alkaline peeling by chemical modification of the REGs was targeted in Papers II and III, in Testova et al. (2012a), and in the unpublished study (Table 3.4). In Paper II and in Testova et al. (2012a), both oxidative (AQ and sodium salt of AQ monosulphonic acid, AQS) and reducing (BH) chemicals were used. In Paper III, only stabilisation with BH was performed due to its higher stabilisation potential.

Table 3.4. Summary of stabilisation conditions applied to different substrates.

Included in	Substrate	Stabilisation chemical	Concentration/ charge	Application
Paper II	Cotton linters after OA treatment	AQ	0.1-1.25 g/L	In-situ (alkaline stage)
		AQS	0-1.5 g/L optimal 0.7 g/L	
		BH	0-3.8 g/L optimal 0.76 g/L	
		BH	0-3.8 g/L	Separate stage, pH 13, 70 °C
Paper III	Birch chips after P170 autohydrolysis	BH	0.5 % o.d. wood	In-situ (pulping)
Unpublished study	Birch chips after P170 autohydrolysis	AQS	0.7 % o.d. wood	In-situ (pulping)
Testova et al. (2012a)	Birch chips after OA prehydrolysis	AQ	0.75 % o.d. wood	In-situ (pulping)
		AQS	0.7 % o.d. wood	
		BH	1 % o.d. wood	
Unpublished study	Raw birch chips	BH	0-5 % o.d. wood	In-situ (pulping)
	Birch chips after OA prehydrolysis	BH		
	Birch chips after P170 autohydrolysis	BH		

3.7 Specifications of the studies not included in the papers

The studies not included in the Papers I-IV are discussed as follows: precipitation of xylan from autohydrolysates (unpublished) (Section 4.3.1); oxalic acid prehydrolysis (Testova et al., 2012a) (Section 4.2); in-situ stabilisation of birch chips and production of paper pulps from OA prehydrolysed wood (Testova et al., 2012a) (Sections 4.4.2, 4.5.2-3); and effect of BH addition on delignification (unpublished) (Section 4.4.2).

3.8 Principal analytical and computational methods

The principal analytical methods are summarised in Table 3.5 More detailed method descriptions can be found in the corresponding papers.

Table 3.5. Overview of the principal analytical methods.

Solid phase	Liquid phase
Quantification of carbohydrates, side chains and degradation products	
Neutral sugars Hydrolysis + HPAEC-PAD (Papers I, III, and IV) *NREL/TP-510-42618, NREL/TP-510-42623*	
Acetic acid Acetic acid kit K-ACET (Megazyme) (Paper I)	
In the solid phase carbohydrates are recalculated according to Janson's formulae (Janson, 1970)	**Sugars, uronic acids** Methanolysis GC (Paper I) (Sundberg et al., 1996)
	Furanic compounds HPLC (Paper I)
Quantification of lignin	
Gravimetrical/Klason lignin (Papers I,III, and IV) *NREL/TP-510-42618, NREL/TP-510-42623*	
Dissolved lignin UV spectrometry at 205 nm (Paper I, III, IV) *Tappi UM 250 1991*	
Pulp kappa number *SCAN-C 1:00*	**Dissolved lignin** UV spectrometry at 280 nm (Paper IV) *NREL/TP-510-42623*
Macromolecular properties and alkali resistance of carbohydrates	
Intrinsic viscosity in CED (Papers II, III, and IV), *SCAN-CM 15:99*	**Molar mass of hemicelluloses** GPC in NaOH (Papers I and IV)
Molar mass of cellulose GPC in LiCl/DMAc (Paper III) MALLS calculation according to (Berggren et al., 2003)	
Pulp alkali resistance (Paper III) *SCAN-C 34:80*	
Structural characterisation of cellulose	**Quantitative and qualitative analysis of xylooligosaccharides**
Crystallinity, crystal dimension, fibrillar structure WAXS, SAXS (Paper II and III) (Leppänen et al., 2009, Penttilä et al., 2010, Tolonen et al., 2011, Penttilä et al., 2013)	**Quantification of oligomers** HPAEC-PAD (Paper I and IV) (Rantanen et al., 2007)
Crystallinity, crystal dimension, aggregate dimension CP/MAS ^{13}C-NMR (Paper III) (Larsson et al., 1997, Wickholm et al., 1998, Chunilall et al., 2010)	**Fingerprinting** MALDI-TOF MS (Paper I)
Cellulose end-groups (Paper II)	**Dissolved solids analysis (Papers I, II)**
Carbonyl groups BCA method (Garcia et al., 1993, Kongruang et al., 2004)	Total organic carbon (TOC)
Carbonyl groups Fluorescence labelling GPC (Röhrling et al., 2002)	
Carboxyl groups Methylene blue method (Davidson, 1948)	
Inorganic analysis	
Ash content (Paper III) *NREL/TP-510-42622*	**Residual alkali** (Papers II and IV) *SCAN-N 33:94*

HPAEC-PAD – high performance anion exchange chromatography – pulsed amperometric detection

HPLC – high performance liquid chromatography
GC – gas chromatography
CED - cupriethylenediamine
LiCl/DMAc – lithium chloride/dimethylacetamide
GPC – gel permeation chromatography
MALLS – multi-angle laser light-scattering detection
WAXS, SAXS – wide and small angle X-ray scattering
CP/MAS ^{13}C-NMR – cross polarisation/magic angle spinning ^{13}C nuclear magnetic resonance
MALDI-TOF MS – matrix assisted laser desorption ionisation – time of flight mass spectrometry

Modelling in Paper II was performed based on the earlier developed pseudo-first order equations for the alkaline peeling and stopping (Haas et al., 1967), as well as alkaline hydrolysis reactions (van Loon and Glaus, 1997, Pavasars et al., 2003). The existing model was extended for the effect of secondary peeling, viz. the peeling at the newly generated REGs as a result of alkaline hydrolysis. Evaluation of the reaction rate coefficients according to the existing and newly-developed model was performed using the FindFit function in Wolfram Mathematica software.

3.9 Product application tests

3.9.1 Papermaking properties (Paper IV and Testova et al. (2012a))

The pulps were refined in a PFI (Papirindustriens forskningsinstitut) mill at 10% consistency to 1500, 3000 and 5500 revolutions (ISO 5264-2:2002). Schopper-Riegler drainability was determined for all refining levels including the non-refined samples (ISO 5267-1:1999). Handsheets with grammage of approximately 60 g/m^2 were prepared using the KCL model machine (ISO 5269-1:2005). Basic papermaking properties were evaluated according to ISO standard methods. Tensile (ISO 1924-2:1994), tear (ISO 1974:1990), wet and dry zero-span strength (ISO 15361:2000), brightness (ISO 2470:1999), grammage (ISO 536:1995), and density (ISO 534:1988) were all measured. Specific values (indices) for the strength properties were calculated.

3.9.2 Dissolving pulp applications (Paper III)

The suitability of the prepared dissolving pulps for viscose and cellulose acetate production was evaluated by laboratory simulation of the respective processes.

3.9.2.1 Viscose-grade pulp

The reactivity of pulps towards xanthation was tested in the standardised Treiber-plant (Treiber et al., 1962, Hüpfl and Zauner, 1966). Pulp samples first underwent steeping in a

18 wt. % NaOH solution at 50 °C to ensure conversion to Na-cellulose I. After steeping, the pulp was pressed (25 bar, 110-140 s) until the cellulose and alkali content reached 34 wt.% and 16 wt.%, respectively. The pressed pulp was shredded and aged (at 37-38 °C, 19 min) until an intrinsic viscosity in the range of 200-300 mL/g was achieved. Xanthation was performed by adding 32 wt. % CS2 and was followed by the dissolution (10 °C, 150 min) and ripening (20 °C, 18 h) of the viscose dope. The resulting dope was characterised by particle counting (P) on a PAMAS device using a light-blocking principle, and by measuring the filter value (F) with the aid of fractionated PVC powder. The higher filterability value corresponded to better viscose filterability meaning that more viscose was filtered until the filter was plugged.

Viscose dope quality in terms of filterability and particle can be divided into the following categories (Sixta et al., 2013):

excellent	F > 550	P < 5.0
very good	450 < F < 550	5.0 < P < 10.0
good	350 < F < 450	10.0 < P < 20.0
satisfactory	200 < F < 350	20.0 < P < 30.0
poor	F < 200	P > 30.0

3.9.2.2 Acetate-grade pulp

The laboratory cellulose triacetate production was adopted from Solvay Rhodia. A bleached pulp sample was mixed with glacial acetic acid and stirred until completely disintegrated. The excess of acetic acid was removed and activation acid containing solution of sulphuric acid in acetic acid was added to the pulp. Upon completion of activation, the acetylation process was started at a controlled temperature of 35 °C by adding acetic anhydride. The reaction completion was controlled by a simplified ball fall viscosity measurement, in which the reaction mixture free outflow time was measured. Reaction was interrupted by adding a solution of sodium acetate, acetic acid and water. The quality parameters measured for the triacetate dope were transmittance, and yellowness. Transmittance was measured using a Turbiscan MA 2000 device. Cellulose triacetate solutions were vacuumed for 5 minutes in a Ø12mm tube before the measurement. Yellowness was measured using a Shimadzu UV-2550 spectrometer. The solution was placed in a 10 mm thick cuvette and vacuumed for 5 minutes. The absorbance was measured at wavelengths of 440 nm and 640 nm. The solution containing 10 mL acetic acid, 5 mL activation acid, and 5 mL acetic anhydride was used as a reference. The yellowness values (*Cy*) based on absorption coefficients (*abs 640 nm* and abs *440 nm*) were calculated with Equation (3.1):

$$Cy = \frac{10^{-abs640nm} - 10^{-abs440nm}}{10^{-abs640nm}} \tag{3.1}$$

3.9.3 Model study of XOS production from polymeric xylan (Paper IV)

Production of XOS by enzymatic hydrolysis was studied on commercial alkali-extracted birch xylan (X-0502; Sigma, Germany) with the commercial food-grade endoxylanase, Pentopan Mono BG (Novozymes, Denmark). Xylan was dissolved in a NaOH solution, neutralised with HCl and dialysed against water. The non-dried xylan suspension was hydrolysed using two enzyme dosages (0.65 and 6.5 mg of enzyme protein/g of xylan) at 60 °C for 4 h. The yields of the hydrolysis products were calculated based on the xylan content in the sample.

3.10 Calculation of heat generation

For economic considerations, heat generation potential of black liquor was calculated for each of the studied processes. First, heat values of the black liquors were calculated knowing the approximate chemical composition of the black liquors and the heat values of the individual constituents: lignin 27 MJ/kg, hemicelluloses 13.6 MJ/kg and carboxylic acids 14.6 MJ/kg. The amount of heat generated was calculated by multiplying the total amount of dissolved solids in the black liquors by their heat values.

4. Results and discussion

4.1 General aspects of xylan isolation (Papers I, III and IV)

Isolation of pure hemicelluloses from lignocellulosic material at commercially attractive yields while maintaining the properties of the remaining cellulosic fraction at a target level is a practical challenge. A variety of methods isolating xylan from lignocellulosic material have been studied. In general, processes of both physical (solvation) and chemical (depolymerisation, degradation, condensation) nature are involved in any of the methods. In alkaline pre-extraction (Paper IV) at low temperatures and high alkalinity direct dissolution dominates over chemical degradation. In this way, polymeric xylan with a low degree of degradation can be obtained. Extraction is, however, accompanied by the cleavage of the acetyl groups which alters the properties of the isolated xylan. Increased temperature facilitates a number of degradation reactions which affect the properties of both xylan and the other components. Low initial alkalinity may lead to a complete consumption of alkali for neutralisation of the released degradation products (Yoon et al., 2011, Lehto and Alen, 2013) and the process may gain features of acid prehydrolysis where hydrolytic cleavage of the glycosidic bonds dominates, resulting in random depolymerisation of carbohydrates. In acid prehydrolysis (Papers I, III, Testova et al. (2012a)), the overall intensity determines the degree of hydrolytic attack whereas the process acidity in particular determines the macromolecular properties of the isolated hemicelluloses at a given yield. The presence of an acid catalyst may lead to near-quantitative hydrolysis of the oligosaccharides to monomers in the liquid phase. The selection of a pre-treatment method and conditions is not only governed by the target properties of the isolated xylan, but also by the properties of the pulp, which can be produced from the wood residue (Papers III, IV, Testova et al. (2012a)). In prehydrolysis conditions, near-quantitative isolation of wood xylan is achievable. The selectivity for xylan, however, decreases with increases in the extent of isolation. When a product with high cellulose purity is required, prehydrolysis is a viable process (Paper III). Alkaline pre-extraction, on the other hand, is limited in the amount of extractable xylan, but allows higher selectivity to be achieved at a given xylan yield, compared to prehydrolysis. As a result, pure xylan product and fibres with excellent papermaking properties can be obtained (Paper IV).

4.2 Selection of pre-treatment conditions (Papers I, III and IV)

Xylan was isolated from birch wood by applying three pre-treatment techniques, autohydrolysis at four intensity levels (Papers I and III), acid prehydrolysis with oxalic acid (Testova et al., 2012a), and alkaline pre-extraction (Paper IV). The conditions selected for isolating xylan from birch wood and the corresponding amounts of isolated xylan and co-dissolved lignin are summarised in Table 4.1.

The autohydrolysis conditions in Papers I and III were selected based on the previous studies by Testova et al. (2009) and Borrega et al. (2013a), respectively. Initially, the selection of the mild P150 conditions in Paper I (Table 4.1) was intended for the production of paper pulps where only limited amount of hemicelluloses can be withdrawn in order to maintain papermaking properties at a high level (Testova, 2006). Prehydrolysis with a more severe P170 intensity (Table 4.1) is in the range typically applied for the production of dissolving pulps (Sixta et al., 2006)

Table 4.1. Comparison of the pre-treatment conditions and the isolation efficiency (Papers I, III and IV).

Denotation		P150	P170	P200	P220	P(OA)	E
Denotation in papers		P200	P1000, P170	P200	P220	P(OA)	E
Paper		I	I, III	III	III	Testova et al. (2012a)	IV
Temperature	°C	150	170	200	220	120	95
Effective time [a]	Min	100	100	13.5	5	90	63
Liquid-to-solid ratio	L/kg	4	4	4	4	4	9.3
P-factor		200	1000	1198	1274	n.a.	n.a.
Log Px_s		3.2	4.2	4.7	5.0	n.a.	n.a.
Chemical		-	-	-	-	OA	NaOH
Charge	% o.d. wood	-	-	-	-	0.05	89
Isolated anhydroxylose[b]	% o.d. wood	4.3	12.8	7. 6	6.5	4.6	7.2
Co-extracted lignin[b]	% o.d. wood	2.7	3.1	n.m.	n.m.	1.5	1.1

[a] Isothermal time and preheating time equivalent to time at the setup temperature.
[b] Total including the share entrapped in wood pores (after complete washing).
E – alkaline pre-extraction
OA – oxalic acid
n.a. – not applicable
n.m. – not measured

In Paper III, three intensities corresponding to different temperatures (P170, P200 and P220 in Table 4.1) were selected to produce dissolving pulps with the content of residual hemicelluloses in a range from 6 to 1.5% while avoiding subsequent cold caustic purification (Sixta, 2006b). The selection of high temperatures (200 and 220 °C) was justified by the resistance of the recalcitrant xylan towards hydrolysis at temperatures lower than 200 °C (Borrega et al., 2011a). With prolonged autohydrolysis, a larger amount of xylan could be dissolved at the expense of cellulose properties in the wood residue and xylose dehydration to furfural.

Optimisation experiments with OA prehydrolysis revealed that the addition of acid leads to near-quantitative hydrolysis of carbohydrates to monomers (Figure 4.1). The extent of monomers formation with equal wood yield loss values depended on the concentration of the acid. The conditions listed in Table 4.1 (OA(P)) were selected as an alternative xylan isolation method to P150 autohydrolysis.

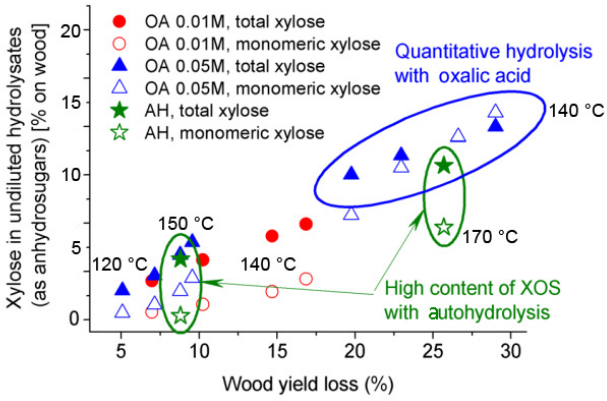

Figure 4.1. Comparison of the monosaccharide share after autohydrolysis and OA prehydrolysis at the same wood yield loss (Testova et al., 2012a). AH – autohydrolysis.

Alkaline pre-extraction allowed transfer of up to a half of the birch xylan into the liquid phase (E-lye) at the temperatures below 100 °C. However, a significant chemical charge of sodium hydroxide had to be applied in order to achieve high selectivity towards xylan. The principal results of alkaline pre-extraction optimisation are presented in Figure 4.2. The effects of temperature and alkali concentration on the amount of extracted anhydroxylose and the absorbance of the E-lye at a wavelength of 280 nm were studied. Xylan dissolution was enhanced as a function of both alkalinity and temperature (Figure 4.2 a, b). However, the difference between the reduction in anhydroxylose content in the solid residue and the amount detected in the liquid phase suggested that at 110 °C and 125 °C a substantial xylan loss through its degradation in alkali occurred (Figure 4.2 c). At the same time, in optimal pre-extraction conditions, lignin retention in the solid phase should remain as high as possible. The highest efficiency of xylan extraction at minimum

lignin co-extraction (absorbance at 280 nm) fell in the area with a low temperature (95 °C) and a high pre-extraction alkalinity (2.5 M) (Figure 4.2).

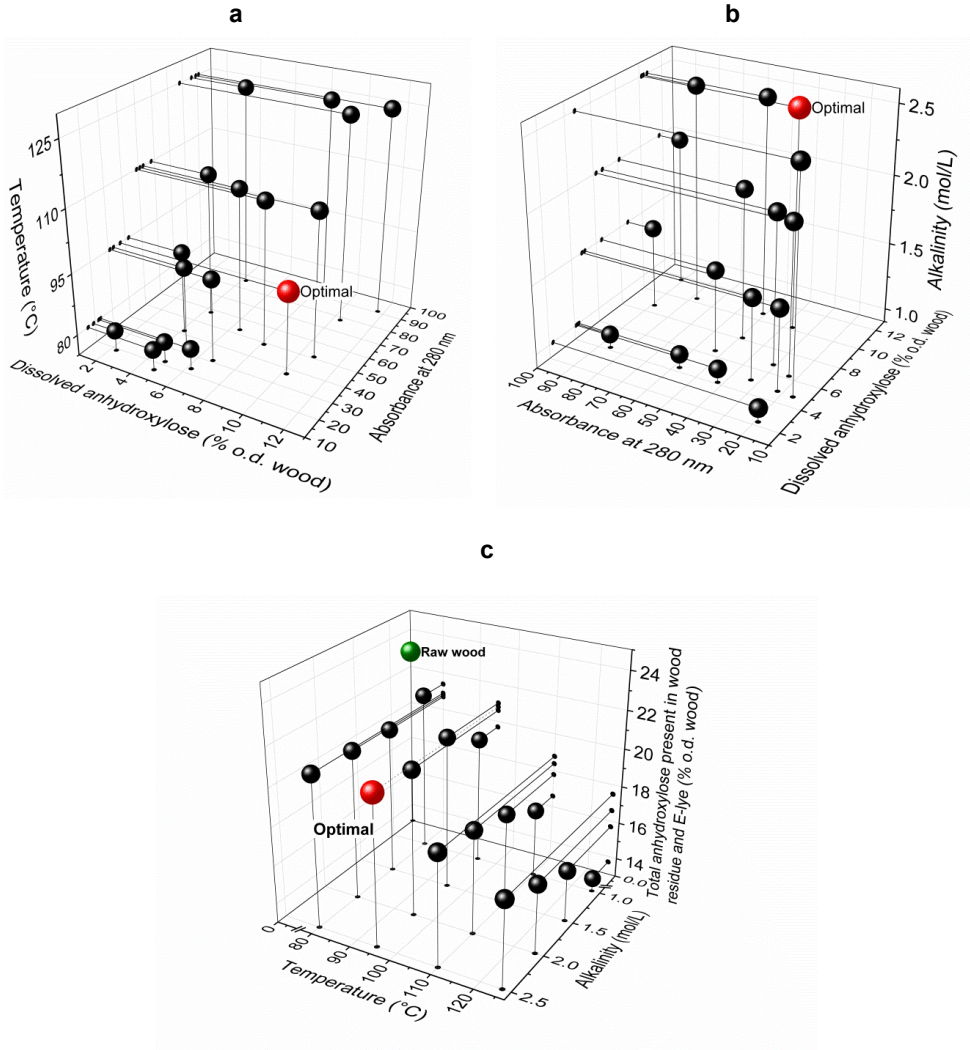

Figure 4.2. The effect of extraction conditions on the amount of anhydroxylose and on lignin absorbance at 280 nm in the E-lye (a and b) as well as on total anhydroxylose present in solid residue and E-lye after pre-extraction (c) (Paper IV). (a) Effect of temperature: the alkali concentration was varied between 1.0, 1.5, 2.0, and 2.5 mol/L. (b) Effect of NaOH concentration: the temperature was varied between 80, 95, 110, and 125 °C. (c) Effect of the pre-extraction temperature and alkalinity on the sum of xylan content in the solid residue and in the E-lye and the solid residue.

Importantly, after any pre-treatment only a share of the liquid phase containing extracted xylan (60-90%) can be recovered. The residual fraction remains in the voids of

the porous wood structure. The completeness of the recovery depends primarily on the temperature and pressure conditions at which the liquid phase is separated from the solid phase. On a laboratory scale, a washing stage was introduced to ensure near-quantitative recovery of the dissolved solids for analytical purposes.

4.3 Isolated xylans (Papers I and IV)

4.3.1 Properties and separation

Properties of the isolated hemicelluloses are strongly dependent on pre-treatment technique and intensity. High-alkalinity pre-extraction produces polymeric xylan effectively free of acetyl groups, which renders it water-insoluble. Xylan isolated from birch wood in alkaline solution had the highest molar mass compared to wood prehydrolysis (Table 4.2) and alkaline post-extraction of bleached pulp (11.7 kg/mol according to Alekhina et al. (2014)).

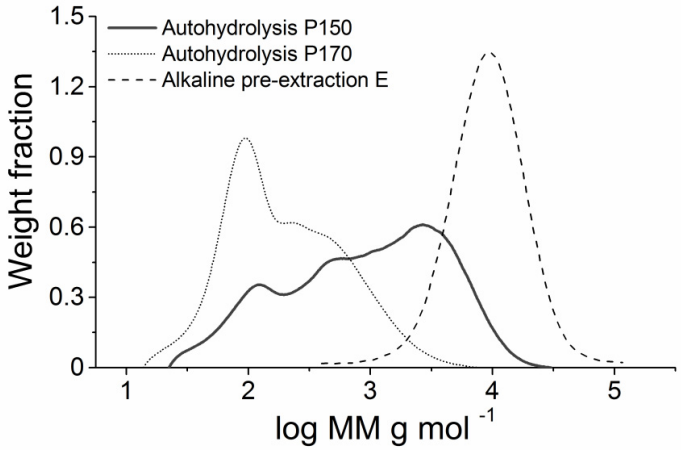

Figure 4.3. Molar mass distribution of the isolated xylan (Papers I and IV).

In acidic conditions, a substantial depolymerisation due to hydrolytic cleavage of glycosidic bonds is observed. Resulting hydrolysates contain hemicelluloses in a wide range of molar masses with the average values notably lower than those in alkaline pre-extraction (Figure 4.3 and Table 4.2). Higher prehydrolysis intensities lead to a substantial hydrolysis of oligomers to monosaccharides with the monomer/oligomer ratio increasing linearly from ~0.06 to 1.3 as a function of intensity in the range of Log Px_s 3.2 (P150) and 5.0 (P220) (Figure 4.4).

Table 4.2. Macromolecular properties of isolated xylans (Paper I and IV).

Sample	Mn kg/mol	Mw kg/mol	PDI
P150	0.3	2.1	7.0
P170	0.1	0.4	4.0
E	10.2	19.8	1.9

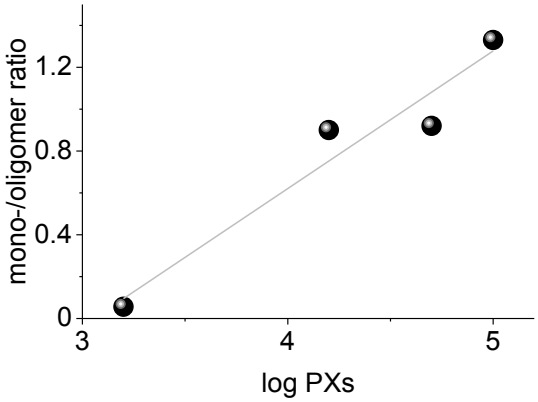

Figure 4.4. The ratio of mono-to-oligomers in wood prehydrolysates as a function of prehydrolysis intensity.

Matrix-assisted laser desorption/ionisation time-of-flight mass spectroscopy (MALDI-TOF-MS) was a valuable tool for fingerprinting the oligomeric composition of the hydrolysates in Paper I. Peaks in Figures 4.5 and 4.6 represent relative abundances of pentosan fragments of different DP. Analyses of pre-separated neutral (Figure 4.5) and acidic (Figure 4.6) fractions of both P150 and P170 samples reveal that the most abundant oligosaccharide species are xylobiose with one acetyl group and xylotriose with one acetyl group and one MeGlcA-substituent, respectively.

In the P150 hydrolysate, both neutral and acidic fractions with DP up to 8 produced strong signals. In the neutral fractions, strong signals were produced by both acetylated and acetyl-free fragments while acidic fragments were mostly acetylated. For the P170 sample the highest peak intensities were observed in the DP range from 2 to 4 in the neutral fraction (Figure 4.5) and from 3 to 6 in the acidic fraction (Figure 4.6). The results obtained by MALDI-TOF-MS, size exclusion chromatography (Figure 4.3) and high performance anion exchange chromatography (HPAEC) (Paper I) confirmed broad distribution of the fragment sizes in the P150 hydrolysate.

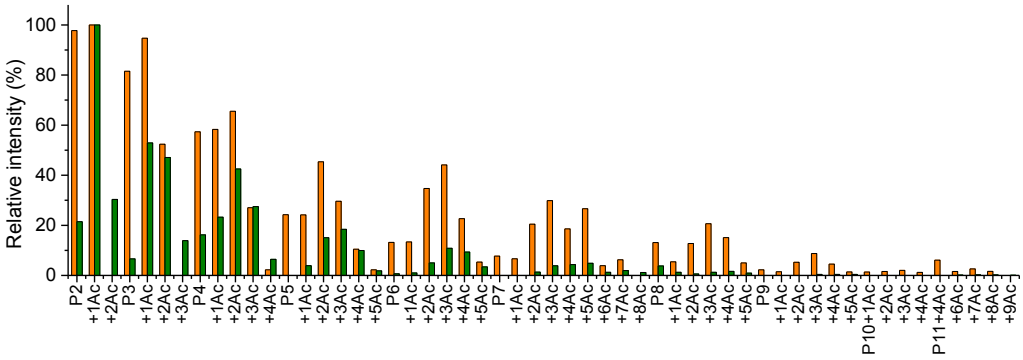

Figure 4.5. MALDI-TOF-MS of neutral pentoses in carbohydrate-containing hydrolysates (P150 – orange bars, P170 – green bars). P corresponds to pentose and the number of carried acetyl groups is marked as nAc (Paper I).

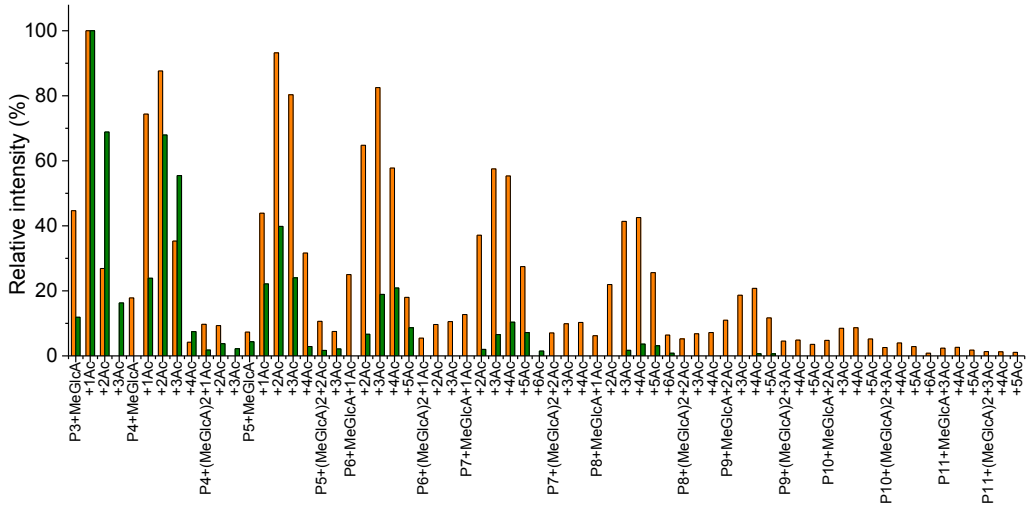

Figure 4.6. MALDI-TOF-MS of acidic pentoses in carbohydrate-containing hydrolysates (P150 – orange bars, P170 – green bars). P corresponds to pentose and the number of carried acetyl groups is marked as nAc (Paper I).

Componential analysis of the P150 and P170 hydrolysates (Table 4.3) complemented the data obtained with MALDI-TOF-MS. Anhydroxylose represented the major share of the liquid phase while the second most abundant constituent was lignin. An increase in prehydrolysis intensity from P150 to P170 was accompanied by only a moderate increase in the amount of solubilised lignin while the anhydroxylose/lignin ratio in the prehydrolysate increased from 1.6 to 4.1. Solubilisation of lignin concerned primarily the acid-soluble lignin fraction in hardwood, as also observed by Leschinsky et al. (2009). Borrega et al. (2011b) reported that a substantial part of acid soluble lignin was solubilised already at low prehydrolysis intensities. The content of HMF in the liquid phase is negligibly small due to the low content of C6-hemicelluloses in birch wood and negligible degradation of cellulose. Furfural formation is quite intensive towards higher

autohydrolysis intensity and accounted for 0.8 g per 100 g of o.d. wood at the P-factor 1000. As reported by Borrega et al. (2011a) for birch wood meal, applying very severe prehydrolysis intensities (log P_{Xs}>6) led to a complete conversion of xylan in the liquid phase to degradation products, primarily to furfural. The liquid phase contained both free acetic acid and acetyl groups bound to the dissolved xylooligosaccharides. The ratio between the free and bound acetic acid increased from 0.54 (P200) to 0.78 (P1000). The average DS of the MeGlcA (0.09) and acetyl groups (0.60) in xylan isolated at P150 was similar to the respective values in the raw wood (0.08 and 0.56). This result suggests that under mild prehydrolysis conditions, dissolved xylan fragments mostly retain their substituents. Further intensification of prehydrolysis led to the continuous hydrolytic cleavage of the substituents in both the solid and the liquid phase.

Table 4.3. Chemical composition of wood and the isolated carbohydrate fractions (undiluted liquor combined with wash filtrate), chemical composition presented in % o.d. wood (Papers I and IV).

		Birch wood	P150	P170	E
Liquid-to-solid ratio	L/kg		4	4	9.3
Anhydroxylose concentration (undiluted)	g/L		10.3	27.0	7.7
Anhydroxylose		26.1	4.32	12.8	7.2
Anhydrogalactose		0.67	0.20	0.63	0.080
Anhydromannose		1.82	0.2	0.68	0
Anhydroglucose		38.3	0.17	0.61	0
Anhydroarabinose		0.34	0.17	0.14	0.024
MeGlcA		3.08	0.55	0.56	n.d.
DS of MeGlcA		0.08	0.09	0.03	n.d.
Free acetic acid		0	0.45	1.25	n.d. (0)
Bound acetyl groups		4.75	0.84	1.59	n.d. (0)
DS of acetylated xylans		0.56	0.60	0.38	n.d. (0)
Furfural		0	0.02	0.80	n.d. (0)
HMF		0	0.01	0.06	n.d. (0)
Total lignin		25.9	2.7	3.1	1.2

n.d. – not determined

n.d. (0) – not determined, but assumed to be zero

The major contaminants in isolated hemicellulose samples irrespective of isolation method are lignin degradation products. Extraction of lignin from wood could be minimised by optimising treatment conditions, for example temperature and alkalinity in Paper IV or replacement of autohydrolysis by acid-catalysed hydrolysis (Testova et al., 2012a). In alkaline pre-extraction, xylan dissolution was clearly enhanced as a function of both alkalinity and temperature (Figure 4.2). Lignin extraction, on the other hand, was mainly affected by the temperature. Based on this observation, the experiment performed at 95 °C in 2.5 M alkali solution had optimal selectivity towards xylan

extraction among the tested conditions. Under mild prehydrolysis conditions, a smaller amount of lignin was detected in the OA prehydrolysis liquid phase than autohydrolysis. Specifically, 1.5% o.d. wood lignin (yield of xylan in the liquid phase 4.6% o.d. wood) was detected in the liquid phase after 0.05 M OA, 120 °C, 90 min prehydrolysis compared to 2.7% for the P150 case (yield of xylan in the liquid phase 4.3% o.d. wood).

Water-insoluble polymeric xylan from alkaline pre-extraction can be separated from the solution by acidification (Sjöström, 1993) or mixing with alcohols (Sihtola and Blomberg, 1974). In Paper IV polymeric xylan was concentrated by applying a sequence of nano- and diafiltration, and isolated from the solution by alcohol precipitation and purification. The major purpose of the membrane filtration stages was to separate the bulk alkali available for process recirculation. Due to the polydisperse nature of lignin and carbohydrates and an overlap in their molar mass distributions, separation of those polymers by means of membrane filtration is inefficient. Furthermore, it is known that the hydrodynamic properties of lignins in dilute solutions are different from those of linear carbohydrates. The molecules of soluble lignins are randomly branched which leads to a reduction of the hydrodynamic dimensions (Karmanov and Monakov, 2001) while hydrated polysaccharides are characterised by large hydrodynamic radii (Dudkin et al., 1991). In addition, the presence of lignin-carbohydrate complexes involving covalent bonding between the polymers limits the possibilities of their physical separation. In the membrane filtration experiments, only a small share of lower molar mass acid-soluble lignin (14% of all dissolved lignin) passed through the 1 kDa membrane. At the same time, precipitation in alcohol efficiently removed the major share of lignin due to its solubility in alcohols while xylan was recovered nearly quantitatively. The final xylan product contained 2.6% o.d. material of lignin, 0.2% o.d. material anhydroglucose and 75.5% of anhydroxylose as measured after sulphuric acid hydrolysis by HPAEC-PAD analysis.

In contrast to the xylan produced under alkaline conditions, prehydrolysis xylan is completely water soluble due to the low molar mass and rather high degree of acetylation. Xylan isolation from prehydrolysates was also attempted (unpublished study). The hydrolysates were first subjected to activated charcoal treatment (Gütsch and Sixta, 2011) for 45 minutes in batch mode at room temperature. Purification was followed by ethanol treatment using 8 parts of ethanol to 1 part of hydrolysate. The ethanol-prehydrolysate ratio of 8:1 was selected in this study to ensure precipitation and needs to be optimised for each prehydrolysate. Only a negligible amount of the dissolved solids was precipitated in the P170 sample due to the low molar mass. In the case of the P150 sample with substantially higher molar mass (Table 4.2), 20% of total dissolved solids were isolated by precipitation. The content of lignin was reduced by 93.2% after activated charcoal treatment. The precipitate contained approximately 60% o.d. powder of anhydroxylose, 15% o.d. powder of other carbohydrates, and only approximately 1% o.d. powder of lignin. The remaining 24% of the dry weight is believed to be represented

by the acetyl and MeGlcA substituents. However, a share of uronic acid substituents may be decarboxylated and remain in the precipitate as a non-detectable functionality. Due to the low precipitation yield, ethanol has limited applicability for separating the carbohydrate fraction from low molar mass hardwood prehydrolysates.

Mild P150 autohydrolysis produced a hydrolysate with the xylan depolymerisation products in a wide range of molar masses (PDI 7.0, Table 4.2) at a rather low extent of xylan isolation (4.3% o.d. wood, Table 4.1). Furthermore, a study on birch prehydrolysis in similar conditions by Testova (2006) revealed lower yield and inferior pulp properties of the prehydrolysis-pulp compared to the reference birch kraft pulp. For these reasons, production of paper pulps after P150 autohydrolysis was not further considered. Instead, oxalic acid-catalysed process yielding prehydrolysates rich in monomeric xylose (Figure 4.1) was believed to be a more feasible solution (Testova et al., 2012a).

4.3.2 Potential products from the isolated xylans

Prehydrolysis and alkaline pre-extraction of birch wood generated xylan-derived products of different yields, structure and properties that determine their further applications.

Polymeric xylan obtained by alkaline pre-extraction in Paper IV had reasonably high molar mass (M_w=19.8 kg/mol) and was effectively free of acetyl groups which rendered the polymer water insoluble. Producing materials from polymeric xylan such as barrier films, porous foams, hydrogels and coatings is seen as an attractive application route (Deutschmann and Dekker, 2012). However, the generally rather low molar mass of wood hemicelluloses makes polymeric applications challenging as compared to cellulose or synthetic polymers. Films prepared from hardwood xylan alone are brittle and become fragmented upon drying due to lack of solubility and possibly due to high glass transition temperature (Gröndahl et al., 2004, Alekhina et al., 2014). The potential of xylan as a substrate for material production can be improved by chemical functionalisation, such as carboxymethylation (Alekhina et al., 2014) or acetylation (Stepan et al., 2013) and cross-linking (Kohnke et al., 2014, Kuzmenko et al., 2014). Xylan can be reinforced by other materials like nanocrystalline cellulose (Kohnke et al., 2014) or mixed with plasticisers like xylitol or sorbitol (Gröndahl et al., 2004) to improve the properties of the materials. Alternatively, polymeric xylan can be applied as an additive in papermaking to enhance product strength (Vaaler, 2008, Silva et al., 2010, Öhman and Danielsson, 2011), which may also require functionalisation. Furthermore, polymeric xylan is regarded as a potential starting material for the production of pure XOS by acid or enzymatic hydrolysis (Deutschmann and Dekker, 2012), which is discussed in Chapter 4.3.3.

Birch wood prehydrolysates depending on the treatment intensities may be rich in XOS, xylose or even degradation products such as furfural. The solutions also contain free

acetic acid which can be recovered as a marketable product. Prehydrolysate obtained by mild prehydrolysis (P150) contains primarily XOS and polymeric xylan with low molar mass. Utilisation of the P150 prehydrolysate with a low yield of removed xylan (4.3% o.d. wood) would require selecting an application with a high added value to compensate for the process costs. Selective enzymatic hydrolysis of the prehydrolysate has the potential to produce rather pure mixture of XOS for food application. Prehydrolysates obtained with the addition of an OA catalyst or under higher prehydrolysis intensity (P170) contain xylose in large quantities (approximately 50%). A near-quantitative selective hydrolysis of the remaining XOS and removal of inhibiting components such as furfural and lignin make it possible to apply fermentation techniques for the production of commodity chemicals and fuels (Helmerius, 2010, Deutschmann and Dekker, 2012) and xylitol (Heikkilä et al., 2005). Under severe prehydrolysis conditions a substantial amount of xylan degradation products is formed as demonstrated by a decrease in the anhydroxylose yield as a result of P200 and P220 prehydrolysis (see Table 4.1 and Borrega et al. (2013b)). Such prehydrolysates may be considered for the production of furfural and its derivatives through dehydration pathway.

4.3.3 Conversion of polymeric xylans to XOS

The high value and growing demand for xylan-derived oligosaccharides motivated a study of XOS production from commercial alkali extracted polymeric birch wood xylan. At the moment, prebiotic application of XOS is in the spotlight of nutritional and medical research. Since prebiotics are non-digestible food additives, the presence of monomeric xylose with high nutritional energy density should be avoided. Acid hydrolysis of polysaccharides inevitably leads to the formation of monomers, while enzymatic hydrolysis in optimised conditions can be performed selectively to produce pure XOS. Pentopan® Mono BG at a charge of 0.65 mg per 1 g of xylan was found to have high selectivity towards the production of XOS. The combined yield of neutral XOS with the DP of 2-4 equalled to 60.5% o.d. xylan. An increase in the enzyme dosage and treatment time facilitated hydrolysis up to 70% of neutral XOS but the share of produced monomeric xylose was simultaneously increased to approximately 5%. Oligosaccharides carrying MeGlcA substituents made a major contribution to the non-quantified fraction, primarily as xylotetraose with MeGlcA at the penultimate non-reducing xylopyranosyl residue. Taking into account the average content of MeGlcA substituents in native birch of 1 unit per 15 xylopyranosyl residues (Teleman et al., 2002, Pinto et al., 2005), the amount of xylotetraose with MeGlcA can be estimated at approximately 25%. The role of the uronic acid substituents in the prebiotic effect of XOS has not been precisely verified. The presence of MeGlcA slowed down fermentation of XOS accompanied by a reduced production of lactate as reported by Kabel et al. (2002). Some positive health effects of uronic acid substituents are currently under discussion (Aachary and Prapulla, 2011).

The promising results obtained in this study on commercial birch xylan suggest viability of enzymatic hydrolysis as a technique to produce XOS. However, further studies involving xylans obtained in the selected alkaline pre-extraction conditions (Chapter 4.2) should be performed in future in order to verify the results.

4.4 Cellulose degradation (Papers II, III, IV, Testova et al. (2012a), and unpublished study)

For a pulping-based biorefinery, preservation of cellulose macromolecular properties and yield is a crucial factor. Despite the stability of highly-ordered cellulose, degradation occurs under any pre-treatment conditions and its extent is a function of the pre-treatment intensity. Acidic prehydrolysis with subsequent alkaline pulping is associated with two degradation pathways of cellulose. In the prehydrolysis stage, hydrolytic cleavage of glycosidic bonds leads to the formation of new reducing ends. In subsequent alkaline pulping, the newly generated REGs initiate alkaline peeling reactions. The extent of acidic degradation can be adjusted by the pre-treatment intensity (temperature, duration, and acidity), whereas alkaline peeling occurs at very low temperatures and proceeds at a high rate, making it difficult to control. Degradation through alkaline peeling can be somewhat reduced by manipulating the functionalities at the reducing end. It can be attempted by modifying them to stable moieties by using oxidative, reductive or derivatising chemicals. The possibility of preserving cellulose yield through the oxidative and reductive pathways were studied using a wide range of chemical charges.

4.4.1 Model study on cotton linters (CL) (Paper II)

The mechanism underlying reductive stabilisation involves conversion of the carbonyl functionality at the reducing end to an alditol structure that is stable against alkaline peeling. Reductive stabilisation of CL after acidic treatment was attempted with BH as a separate stage preceding alkaline degradation and in-situ with the alkaline degradation step. In-situ stabilisation resulted in a superior yield gain of up to 13 %units compared to 9 % units in the separate stabilisation stage (Figure 4.7). The addition of AQ to the alkaline degradation stage slightly reduced the stabilisation effect of BH, due presumably to the reactions between the stabilisation chemicals competing with the reactions at the reducing ends. Oxidative stabilisation involves conversion of the carbonyl group at the reducing end to carboxyl functionality. When oxidative stabilisation with AQ and AQS were studied, the latter demonstrated higher stabilisation potential due to its water solubility and higher redox potential (Evstigneev and Shalimova, 1985). When the reductive and oxidative stabilisation pathways are compared, similar result of the stabilisation with AQS was achieved at lower molar concentrations than with BH. This is

likely to be related to the ability of AQ and its derivatives to regenerate, while BH is irreversibly consumed and can be easily degraded.

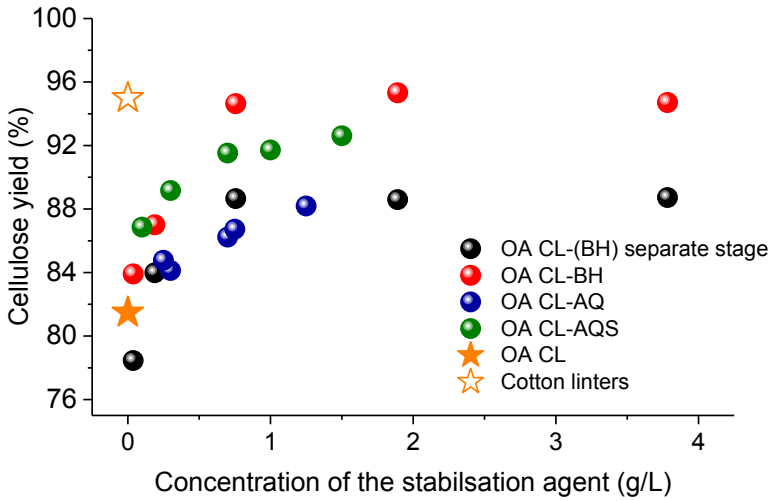

Figure 4.7. The effect of stabilisation chemicals on the cellulose yield after alkaline degradation (Paper II).

In order to confirm chemically the claimed stabilisation effect at the REGs, the behaviour of the functionalities was evaluated after different treatments. The reciprocal value of cellulose DPn could be used as an estimate of the total amount of the reducing ends, regardless of the functionality carried. Fluorescence labelling combined with gel permeation chromatography (GPC) was found to provide the most reliable quantification of the total amount of carbonyl groups. This method was used for modelling purposes where the peeling rate constant is proportional to the initial content of the REGs.

The BCA (bicinchoninic acid) method (Kongruang et al., 2004) was used to monitor changes in the content of the carbonyl groups in all degradation series at 160 °C. The rapid decrease in both carbonyl group content (Figures 4.8, 4.11) and the cellulose yield suggested that all primary peeling occurs in the initial alkaline degradation phase. The lowest content of the REGs was observed when stabilisation agents were applied. The carboxyl group content (Figure 4.9) doubled with AQS stabilisation due to the conversion of the REGs to aldonic acid groups. In the case of BH stabilisation, REGs were converted to alditols the content of which was not measured but was assumed by the difference between the reciprocal DPn values and the sum of the carbonyl and carboxyl group content (Figure 4.10). An increase in carboxyl group content was observed for all data series which was attributed to the formation of MSA as a result of chemical stopping reaction. Furthermore, alkaline hydrolysis generating new REGs resulted in an increase in the overall content of the reducing ends.

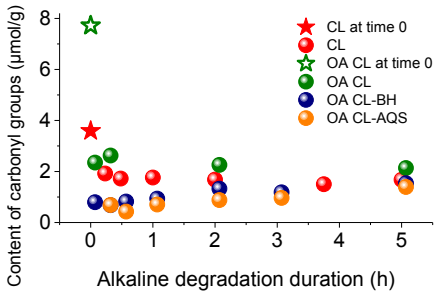

Figure 4.8. The content of the carbonyl groups in the CL samples as a function of alkaline degradation duration at 160 °C (Paper II).

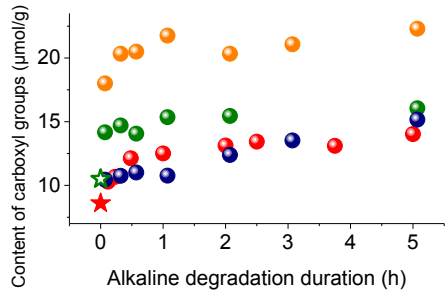

Figure 4.9. The content of the carboxyl groups in the CL samples as a function of alkaline degradation duration at 160 °C (Paper II).

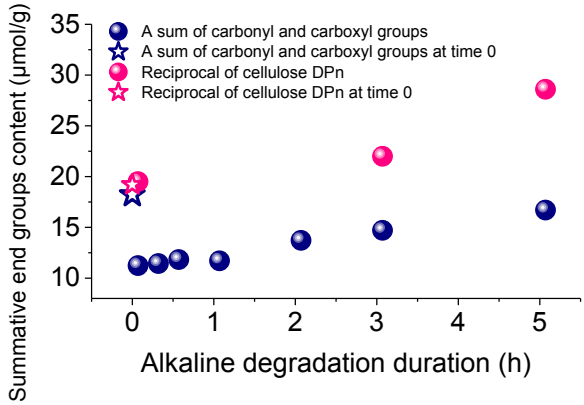

Figure 4.10. Reciprocal DPn and the sum of the carbonyl and carboxyl groups in the CL samples pre-treated with oxalic acid and stabilised in-situ with BH. The difference between the curves indicates the formation of alditols (based on Paper II).

For the kinetic study, degradation series at two temperatures, 125 and 160 °C were conducted using untreated CL, OA pre-treated CL without stabilisation and with in-situ stabilisation with AQS and BH. The BH and AQS concentrations were selected to ensure similarly high cellulose yield of 90-92% after alkaline degradation.

The cellulose yield loss data series were first fitted to an existing model for cellulose degradation expressed by van Loon and Glaus (1997) and Pavasars et al. (2003) based on the previous studies by Haas et al. (1967) and Lai and Sarkanen (1967):

$$D = 1 - \left(1 - \left(\frac{k_p}{k_s} R_0 \left(1 - e^{-k_s t}\right)\right)\right) e^{-k_h t}, \qquad (4.1)$$

where D is the overall carbohydrate yield loss, t is the reaction time, k_p, k_s, and k_h stand for the peeling, stopping and alkaline hydrolysis reaction rates coefficients, respectively, and R is the mole fraction of the REGs at time 0.

The traditional model (Equation 4.1) included the three rate constants typical for cellulose degradation. However, the secondary peeling resulting from the REGs formed as a result of alkaline hydrolysis was not accounted for. To extend the model, a term denoting cellulose degradation resulting from secondary peeling was included. Such a model can be expressed by the following system of differential equations:

$$\begin{cases} \dfrac{dR}{dt} = -k_s R + k_h\left(\Gamma_0 - P - H\right) & (4.2) \\ \dfrac{dP}{dt} = k_p R & (4.3) \\ \dfrac{dH}{dt} = k_h\left(\Gamma_0 - P - H\right) & (4.4) \end{cases}$$

where Γ_0 stands for the amount of initial material, R for the mole fraction of the REGs, P the mole fraction of peeled off material, and, H the mole fraction of degraded material through hydrolysis. In Equation 4.2 the decrease in REGs due to the stopping reaction is proportional to the amount of REGs and the increase in REGs due to hydrolysis is proportional to the amount of non-degraded material. Equation 4.3 expresses that the material is being peeled off at a rate proportional to the amount of REGs. According to Equation 4.4, the degradation rate due to hydrolysis is proportional to the amount of non-degraded material.

The system of Equations 4.2-4.4 can be solved with the DSolve function of the Wolfram Mathematica software to yield:

$$D = \Gamma_0\left(1 - \left(1/2 + \gamma\right)\exp\left(-\left(\alpha + \beta\right)t\right) - \left(1/2 - \gamma\right)\exp\left(\left(\alpha - \beta\right)t\right)\right), \quad (4.5)$$

with

$$\begin{cases} \alpha = \frac{1}{2}\sqrt{\left(k_s - k_h\right)^2 - 4k_h k_p} \\ \beta = \frac{1}{2}\left(k_h + k_s\right) \\ \gamma = \dfrac{k_h + 2\rho_0 k_p - k_s}{2\sqrt{\left(k_s - k_h\right)^2 - 4k_h k_p}} \end{cases} \quad (4.6)$$

The data fits with the high coefficients of determination were produced with both traditional (Equation 4.1) and the newly developed (Equation 4.5) models (Figure 4.11 and Table 4.4). However, due to the limited number of data points in the initial

degradation stage, large relative standard errors (Table 4.4) were found for the linearly correlated peeling and stopping rate constant estimates. Because of this correlation, the ratio between the peeling and stopping reaction rate constants is considered to be a more reliable value.

Stabilisation with both BH and AQS resulted in decreased peeling-stopping ratios compared to those without stabilisation (Table 4.4). The magnitude of the hydrolysis rate constant was the largest for AQS stabilisation series compared to the other series. This behaviour could be caused by the oxidation of primary hydroxyl groups in anhydroglucose units, which could render the adjacent glycosidic bond more reactive towards alkaline hydrolysis.

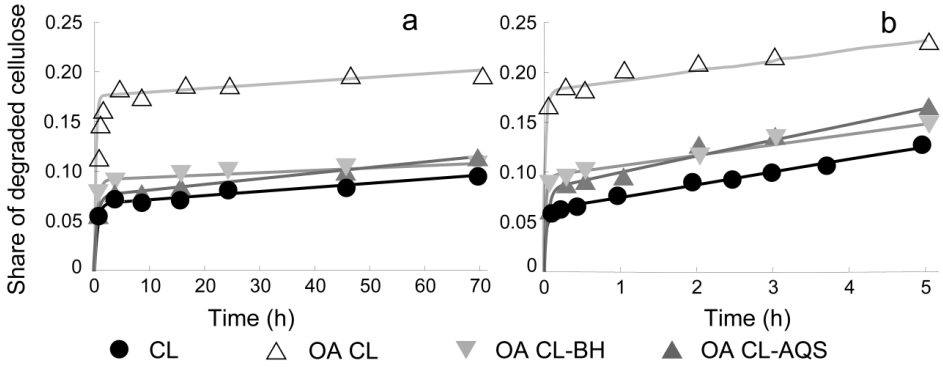

Figure 4.11. Data fits to the developed model for alkali degradation at 125 °C (a) and 160 °C (b), L:S=40 mL/g, NaOH 20 g/L, AQ 0.1 g/L, BH and AQS concentrations in the respective series 0.76 and 0.7 g/L (Paper II).

Table 4.4. Rate constants and standard errors for reactions of cellulose in an alkaline environment calculated by applying the developed model (Equation 4.5) and the traditional model (Equation 4.1) (values in parentheses) (Paper II).

	Reaction temp., °C	Cotton linters	CL treated with OA		
			no stabilisation	stabilisation with BH	stabilisation with AQS
k_p, h^{-1}	125	200±35	327±26	83±13	29±10
		(199±35)	(327±26)	(83±13)	(29±10)
	160	2719±1232	3172±608	1899±745	697±173
		(2696±1231)	(3166±607)	(1893±744)	(688±173)
k_s h^{-1}	125	1.8±0.3	3.9±0.4	1.9±0.3	1.1±0.4
		(1.8±0.3)	(3.9±0.4)	(1.9±0.3)	(1.1±0.4)
	160	26±13	37±7	41±17	17±5
		(26±13)	(37±7)	(41±17)	(17±5)
$k_h \times 10^4$, h^{-1}	125	0.040±0.007	0.053±0.016	0.059±0.019	0.32±0.07
		(4.5±0.6)	(4.6±1.2)	(2.6±0.8)	(9.3±1.4)
	160	1.3±0.1	1.4±0.3	2.5±0.5	4.5±0.7
		(140±9)	(130±21)	(120±17)	(190±22)
k_p/k_s	125	111	84	44	26
		(111)	(84)	(44)	(26)
	160	105	86	46	41
		(104)	(85)	(46)	(40)
$k_p/k_h \times 10^{-7}$	125	5.0	6.2	1.4	0.09
		(0.044)	(0.071)	(0.032)	(0.0031)
	160	2.1	2.2	0.75	0.15
		(0.019)	(0.024)	(0.016)	(0.0036)
R^2	125	0.999	0.999	0.999	0.995
	160	0.999	0.999	0.998	0.997

R^2 – coefficient of determination

Both models produced very similar estimates for peeling and stopping rate constants (Table 4.4). The major difference was observed in the alkaline hydrolysis rate constant where the values calculated with the developed model were by two orders of magnitude smaller than those in the traditional model since in the developed model alkaline hydrolysis has significance for the amount of degraded cellulose only through creating new REGs. The validity of the developed model was confirmed by the calculation of the chain scission rate constant (Equation 4.7) closely associated with alkaline hydrolysis.

$$\frac{1}{DPv_t} - \frac{1}{DPv_0} = k_{CS} t \,, \tag{4.7}$$

where k_{CS} is the rate constant for hydrolytic chain scission, DPv_t intrinsic viscosity-derived DP (DP_v) at time t of alkaline degradation, DPv_0 is the starting DPv and $\frac{1}{DPv_t} - \frac{1}{DPv_0}$ is the number of chain scission per anhydroglucose unit at time t.

The chain scission rate constant values k_{CS} resembled the alkaline hydrolysis rate constant estimates obtained by the developed model. For example for OA pre-treated CL a k_{CS} value of 1.8×10^{-4} h^{-1} was obtained which resembled the k_h value of 1.4×10^{-4} h^{-1} obtained with the developed model rather than the value of 130×10^{-4} h^{-1} with the traditional model.

4.4.2 Stabilisation experiments with wood (Paper III, Testova et al. (2012a), and unpublished study)

The selected stabilisation conditions (Table 3.4) were applied to the birch chips after OA and P170 prehydrolysis (Table 4.5). The stabilisation additives increased the yield of xylan along with the yield of cellulose, confirming the low selectivity of the additives towards cellulose. Furthermore, the relative yield increase of xylan was higher compared to that of cellulose, which was presumably caused by higher accessibility of the hemicelluloses to stabilisation chemicals. Paper pulp stabilised with BH also contained 0.8% o.d. wood of glucomannan while in the other pulps glucomannan was not detected.

Unselective stabilisation of wood carbohydrates is beneficial in the case of paper pulps where the content of hemicelluloses is important for papermaking properties. However, the stabilisation of hemicelluloses contradicts the goal of dissolving pulp manufacture, namely to minimise the content of hemicellulose while preserving the cellulose yield (Paper III).

In the experiments with birch chips, a reduced delignification rate upon the addition of BH was observed (Table 4.5). Longer pulping durations were required to reach the target degree of delignification (kappa numbers). For the wood residue after P170 autohydrolysis, however, such behaviour was not observed. There, stabilisation with BH and AQS performed at the same pulping intensity resulted in pulps with similar kappa numbers.

Table 4.5. Pulp production from birch chips under various pre-treatment and stabilisation conditions (Paper III, Testova et al. (2012a)).

Pre-treatment	Stabilisation additive		H-factor	Yield, %	Kappa number	Xylan[1], % o.d.wood	Cellulose[1], % o.d. wood	GM[1,2], % o.d. wood
	type	charge, % o.d. wood						
No	-	-	800	51.0	17.3	13.6	36.3	0
OA	-	-	400	42.7	19.8	6.4	34.7	0
OA	AQ	0.75	350	44.3	15.6	7.1	35.8	0
OA	AQS	0.7	450	45.5	16.0	7.3	36.8	0
OA	BH	1	750	46.3	16.1	7.9	36.4	0.8
OA	BH	1	400	n.m.	26.7	n.m.	n.m.	n.m.
P170	-	-	350	36.9	8.3	2.2	34.0	0
P170	AQS	0.7	300	37.4	8.6	2.3	34.4	0
P170	BH	0.5	300	38.3	8.2	2.8	34.8	0

[1] Carbohydrates calculated according to Janson's formulae (Janson, 1970)
[2] GM - glucomannan
n.m. – not measured
OA - Oxalic acid treatment at 0.05 M, 120 °C, 90 min
P170 – Autohydrolysis at 170 °C for 100 min

In order to verify the observation, a separate set of experiments was performed to investigate the effect of sodium borohydride addition on the pulping results of raw birch chips and chips after OA and P170 prehydrolysis (Table 4.6). The results confirmed the observation of the effect of BH concentration on wood delignification. The effect was particularly expressed for the oxalic acid pre-treated chips where the kappa number and the amount of the rejects increased significantly at the highest charges of BH applied (Table 4.6). However, at the highest BH charge of 5%, an increase in kappa number was also observed for the raw wood and P170 pre-treated wood (Table 4.6). In the experiments performed, the pulping H-factors were selected according to Table 4.4 for the analogous pre-treatment conditions except that in the case of P170 the H-factor was further decreased to from 300 to 200 (Table 4.6). H-factor series performed for the OA pre-treated wood without BH addition and with 5% addition (Figure 4.12) suggest that the difference in kappa number as a function of BH charge is diminished at higher pulping intensities and, consequently, low kappa numbers. The smaller observed effect of BH addition in the raw wood and P170 series might be attributed to the lower level of kappa numbers than in the case of P(OA) (kappa numbers at BH 0% 14.9, 7.5 and 18.2, respectively).

Table 4.6. In-situ stabilisation of birch chips with sodium borohydride after various pre-treatment and stabilisation conditions (unpublished study). Pulping was performed at 160 °C, alkali charge 22% o.d. wood, and with AQ charge of 0.1% o.d. wood.

Raw material	$NaBH_4$ charge	H-factor	Total yield	Screened yield	Rejects	Kappa number	Residual alkali	Total lignin	Xylan	Glucomannan	Total carbohydrates
	%		%	%	%		g/L	% of raw wood			
Birch wood	0	800	52.0	51.9	0.04	14.9	11.5	1.59	13.9	0	50.4
	0.1		54.0	53.7	0.12	14.9		1.47	14.3	0	52.3
	0.35		53.6	53.6	0.02	14.2		1.33	14.2	0	52.2
	0.7		51.9	50.9	0.02	13.9		1.30	12.9	0.75	50.6
	1		52.9	52.9	0.00	14.4	13.0	1.19	12.9	1.04	51.8
	1.5		51.2	51.2	0.00	14.1		1.29	12.1	1.59	49.9
	3		50.2	50.2	0.01	16.0		1.50	11.5	1.60	48.7
	5		53.1	53.1	0.03	19.2	13.9	1.85	12.4	1.64	51.3
P(OA)	0	400	43.9	42.2	0.88	18.2	10.1	1.29	7.1	0	42.5
	0.1		44.3	42.7	1.59	19.9		1.49	6.8	0	42.7
	0.35		43.3	42.4	0.66	18.0		1.59	7.1	0	41.7
	0.7		44.6	43.9	0.53	15.7		1.53	7.2	0.55	43.1
	1		44.3	43.8	0.53	16.4	18.1	1.40	7.2	0.90	42.9
	1.5		45.7	45.1	0.63	17.1		1.57	7.3	1.08	44.1
	3		44.7	43.7	0.96	20.6		1.80	7.0	1.08	42.8
	5		45.6	42.3	3.33	25.3	22.9	2.14	7.3	1.42	43.3
P170	0	200	34.4	34.4	0.00	7.5	19.1	0.73	1.9	0	33.7
	0.35		35.1	35.1	0.00	7.2		0.76	2.5	0	34.3
	0.7		36.5	36.5	0.03	7.3		0.80	3.1	0	35.7
	1		38.7	38.7	0.00	7.1	29.0	0.88	3.3	0	37.8
	1.5		39.9	39.8	0.06	7.4		0.81	3.3	0.50	39.1
	3		41.9	41.9	0.00	7.4		0.70	3.5	0.70	41.1
	5		41.8	41.8	0.00	8.3	33.0	0.82	3.8	0.74	41.1

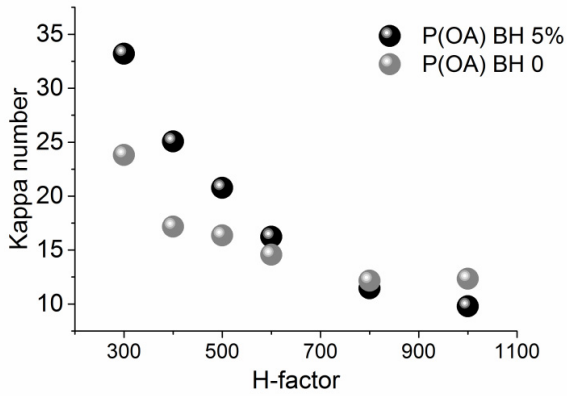

Figure 4.12. Kappa number of the oxalic acid pre-treated pulps without the addition of sodium borohydride or with 5% addition as a function of pulping H-factor (unpublished study).

The inhibitory behaviour of BH towards delignification may be related to the interaction of BH with AQ in SAQ pulping, which may interfere with the redox cycle of AQ. It is known that both reductive and oxidative reactions of lignin with AQ are important for lignin fragmentation (Sixta et al., 2006). In the presence of BH, the oxidative effect of AQ towards lignin may be weakened due to a preferred reaction with BH. On the other hand, lignin structures with functionalities in the alpha-carbonyl position play an important role in lignin fragmentation in alkaline conditions (Sixta et al., 2006). Therefore, reduction of the carbonyl groups in lignin with BH (Sarkanen and Ludwig, 1971) could render lignin more resistant to fragmentation.

The results in Table 4.6 also demonstrate that by far the highest carbohydrate stabilisation efficiency occurred in the case of P170, though significant stabilisation of glucomannan was observed for all stabilisation series (Table 4.6). This is in an agreement with the results in Table 4.5. The initial glucomannan content in birch wood was 2.5% (Paper IV), so it was possible to preserve up to 64% of the total amount of glucomannan by introducing BH. This finding could be of an interest for the stabilisation of softwoods where the impact of the glucomannan yield is more pronounced.

4.4.3 Cellulose degradation in E-SAQ process (Paper IV)

In alkaline pre-extraction, the extent of cellulose degradation is a function of alkaline extraction conditions. The optimisation experiments of the alkaline pre-extraction demonstrated that pre-extraction temperature had the highest effect on the retention of cellulose in the solid phase (Figure 4.13). Physical dissolution of xylan occurring at low temperatures gradually develops into chemical reactions of alkali with all wood constituents when the temperature is increased. Therefore, at the 80 and 95 °C only minimal degradation of cellulose is observed compared to the initial content of 39.8%

o.d. wood (Figure 4.13), while the yield loss is observed mainly through xylan dissolution. When higher temperature at the same treatment duration is applied, the overall intensity of the chemical attack increases. Under more severe pre-treatment conditions of 110 and 125 °C, a substantial degradation of both xylan and cellulose is observed (Figure 4.14). The involvement of cellulose peeling reactions was supported by the fact that under all applied pre-extraction conditions, the extract contained negligible amounts of anhydroglucose (up to 0.15% o.d. wood), which likely originated from the extracted polymeric glucomannan. Despite the fact that at higher temperatures the ratio between alkaline peeling and stopping reaction rates decreases due to the higher activation energy of the stopping reaction (Sixta et al., 2006), the overall severity of the process (temperature and duration) determines the share of degraded carbohydrates in these experiments.

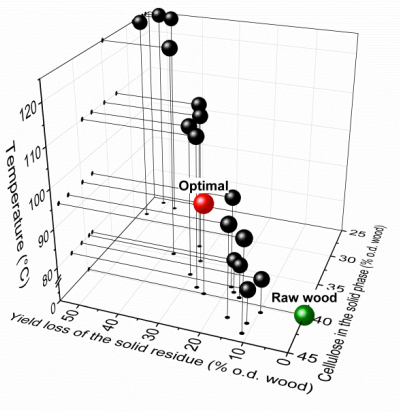

Figure 4.13. Retention of cellulose in the solid phase and the yield loss of wood as a function of pre-extraction temperature.

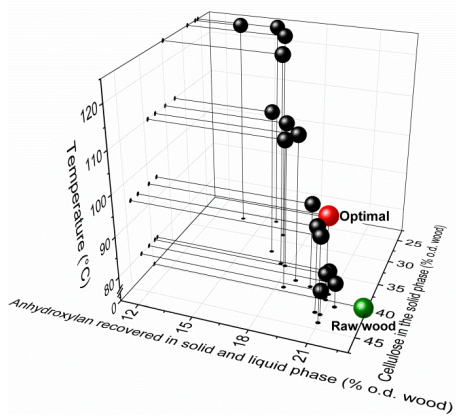

Figure 4.14. Retention of cellulose in the solid phase and the total recovered anhydroxylose a function of pre-extraction temperature.

4.5 Production of hemicellulose-lean pulps (Papers III and IV, and Testova et al. (2012a))

4.5.1 Wood residues for pulp production

Pulping was carried out using wood residues without intermediate washing except for the alkaline pre-extraction residue, where a washing stage with a liquid-to-solid ratio of 1.2 L/kg was carried out to reduce the alkalinity of the pulping stage, as discussed in Chapter 4.5.2.

Both autohydrolysis and alkaline pre-extraction were accompanied by the formation of chromophores through the reactions of phenolic lignin species. The resulting structures were responsible for the colour change of the pre-treated chips (Figure 4.15).

a b c d

Figure 4.15. Birch chips after pre-treatments, where: (a) are untreated chips; (b) – chips after prehydrolysis with oxalic acid (P(OA)); (c) – chips after prehydrolysis at a P-factor 1000 (P170); (d) – chips after alkaline pre-extraction. Photograph (d) by Luciana Costabel (2013).

Along with the formation of condensed lignin structures, depolymerisation of lignin in prehydrolysis resulted in its increased reactivity and solubility in organic solvents (Figure 4.16) (Testova et al., 2009). This phenomenon was extensively studied by Lora and Wayman (1978b). The authors reported that autohydrolysis rendered lignin partly soluble in organic solvents such as dioxane-water mixture and in diluted caustic solutions. The solubility depended on the autohydrolysis intensity and reached a maximum at such intensities where lignin depolymerisation was extensive and condensation reactions occurring at high intensities were still weakly pronounced. In the present study, a significant amount of lignin could potentially be isolated from the wood residue by solvent extraction (11.3% o.d. wood in the case of P170 wood residue when extracted with acetone).

Figure 4.16. Extraction of prehydrolysed wood residue (P170) with acetone.

4.5.2 Basic pulp properties

In a pulping based biorefinery, producing high-quality pulps comparable or even superior in properties to the conventionally-produced equivalents is a priority. Insofar as paper pulps are concerned, papermaking properties are of critical importance, while for the dissolving pulps, cellulose purity and processability into certain products must be ensured. Maximising pulp yield is an important economic aspect for any pulping process.

In the pre-treatments aiming at the isolation of hemicelluloses, cellulose is also affected. Depolymerisation and dissolution of cellulose are typically associated with one another and occur concurrently to a different extent. Depolymerisation dominates in acidic environments as a result of hydrolytic cleavage of glycosidic bonds, while dissolution prevails in alkaline conditions. During prehydrolysis, the cellulose yield remains at a fairly high level. The difference in cellulose yield between the samples increases as a function of prehydrolysis intensity in subsequent alkaline pulping where endwise peeling reactions occur (Table 4.7).

After mild and selective pre-treatments of birch wood, the pulp yield is primarily a function of residual xylan content (Table 4.7). Under more severe pre-treatment conditions (P170-P220), a significant cellulose yield loss is also observed. The highest pulp purity (cellulose content of 98.6%) was obtained in the case of P220 prehydrolysis (Table 4.7). This, however, was only achievable at the expense of the cellulose yield, with half of the initial cellulose lost in the prehydrolysis, pulping and bleaching operations. On the other hand, alkaline pre-extraction in optimised conditions combined with SAQ pulping (E-SAQ) did not affect the content of cellulose to a greater extent than pulping of untreated wood did (SAQ).

Prehydrolysis and alkaline pre-extraction have different potential in terms of achievable pulp properties. Prehydrolysis allows near-quantitative removal of xylan at high treatment intensities due to the low resistance of recalcitrant fractions towards hydrolysis at high temperatures (Borrega et al., 2013a). Furthermore, after prehydrolysis followed by alkaline pulping the primary layer of the cell wall is almost completely removed and the S1 secondary wall is partly removed (Sixta, 2006a), which affects the swelling ability and the accessibility of the fibre wall to chemicals. On the other hand, it was demonstrated that prehydrolysis performed even under mild intensities has an adverse effect on the papermaking properties of pulps (Testova, 2006, Schild et al., 2010). The characteristics noted reveal the preferred use of prehydrolysis for the production of dissolving pulps. In a fully alkaline pre-treatment pulping sequence the outer cell wall layers are preserved to a greater extent (Schild and Sixta, 2011). The share of xylan that can be extracted during alkaline pre-extraction is limited and production of dissolving pulps would require additional purification step after pulping. Schild and Sixta (2011) reported that the xylan content of the eucalyptus SAQ pulp pre-extracted with alkali was high (6.5%) even when cold caustic post-extraction was applied. The

performance of such pulp was poor in a viscose filterability test, yielding viscose dope with a filter value of 139 and particle count of 50.3 ppm. A the same time, a number of research groups demonstrated that pulps with excellent papermaking properties can be produced by pre-extraction pulping (Al-Dajani and Tschirner, 2008, Schild et al., 2010, Yoon et al., 2011). Alkaline pre-extraction, therefore, favours production of paper pulps.

Table 4.7. Pre-treatment and pulping conditions and pulp properties (Papers III, IV, Testova et al. (2012a)).

Pulp name		SAQ	P(OA)-SAQ	P(OA)-SAQ-AQ	P(OA)-SAQ-AQS	P(OA)-SAQ-BH	E-SAQ	P170	P170-BH	P200	P220
Pulp grade		Paper						Dissolving			
Pre-treatment conditions											
Pre-treatment		n.a.	Oxalic acid 0.05 M				E	Autohydrolysis			
Temp., °C		n.a.	120				90	170		200	220
Effective time		n.a.	90				63	100		13.5	5
Pulping conditions											
H-factor		800	400	350	450	750	550	350	300	200	200
AQ charge	% o.d. wood	0.1	0.1	0.1	0.1	0.1	0.075	0.1			
Effective alkali		20	20	20	20	20	19.1	22			
Stabilisation		n.a.	n.a.	AQ	AQS	BH	n.a.	n.a.	BH	n.a.	n.a
- charge	% o.d. wood	n.a.	n.a.	0.75	0.7	1	n.a.	n.a.	0.5	n.a.	n.a.
Pulping results		Oxygen delignification						Bleaching			
Yield	% o.d. wood	49.6	41.9	43.3	44.6	46.0	44.7	34.1	36.2	30.3	22.9
Xylan content[1]	% o.d. wood	12.5	6.1	6.5	7.0	8.0	9.0	2.0	2.6	0.85	0.32
	% pulp	*25.3*	*14.6*	*15.1*	*15.8*	*17.4*	*20.1*	*5.8*	*7.2*	*2.8*	*1.4*
Cellulose content[1]	% o.d. wood	36.0	34.7	35.7	36.6	36.4	35.8	32.1	33.5	29.5	22.6
	% pulp	*72.5*	*82.9*	*82.4*	*82.0*	*79.1*	*80.1*	*94.2*	*92.8*	*97.2*	*98.6*
Intrinsic viscosity	mL/g	945	1147	1112	1153	1104	878	507	572	432	307
Kappa number		13.1	12.9	10.6	11.3	9.0	12.1	0.8	0.8	0.7	0.7

[1] Carbohydrates calculated according to Janson's formulae (Janson, 1970).
E – alkaline pre-extraction
n.a. – not applied

4.5.3 Paper pulps (Paper IV and Testova et al. (2012a))

Paper-grade pulps were produced using a pre-treatment combined with SAQ pulping in a sequence. Mild isolation of xylan was selected to preserve cellulose properties and yield to a maximum extent and to maintain papermaking properties at a reference level. Unlike in dissolving pulps, high hemicellulose content in paper pulps has a positive impact on the final product through enhanced fibre bonding, strength properties, surface smoothness, and decreased bulk and porosity (Silva et al., 2010). In accordance with these findings, only a certain share of the hemicelluloses can be withdrawn from wood prior to pulping without a major impact on the quality. To achieve the targets, the yield loss of birch wood after pre-treatment was limited to a maximum of 10% for acid prehydrolysis and 25% for the more selective alkaline pre-extraction. One reference SAQ pulp and five pulps with a pre-treatment were produced and characterised (Table 4.7). Despite the stabilisation effort and the optimisation of pulping conditions the target yield of a reference SAQ pulp was not achieved for either alkaline pre-extracted or OA prehydrolysed pulps. The reasons for the reduced yield, as indicated by the carbohydrate balance, are the lower xylan content and, to a much lesser degree, degradation of cellulose. This implies that after isolating a share of xylan by a pre-treatment, the remaining hemicellulosic fraction is still susceptible to degradation in pulping conditions. In the case of alkaline pre-extraction, however, yield optimisation potential related to the alkali charge of the pulping stage has not been fully covered by the present study.

The E-SAQ pulping process had to be optimised in terms of alkali charge in order to achieve acceptable yield since the starting alkali charge in pre-extraction was as high as 89% o.d. wood (Figure 4.17). High concentration of effective alkali in pulping conditions promotes random cellulose chain scission initiating secondary peeling reactions. Pressure discharge of alkali from the reactor after completing pre-extraction was not solely sufficient to obtain an alkali charge suitable for pulping. Intermediate washing at a liquid-solid ratio of 1.2 L/kg enabled increasing the pulp yield from 35.4 to 46.6% o.d. wood. The overall alkali consumption of the E-SAQ process was found to be 15.7 % o.d. wood, which was lower than the 18% o.d. wood of the reference SAQ (Figure 4.17). Higher summative retention of carbohydrates in the E-SAQ process (in pulp and pre-extract) was the likely reason for the lower alkali consumption. Scenarios for enhancing the yield of the E-SAQ process might be further reduction of the alkali charge or decreasing the cooking temperature.

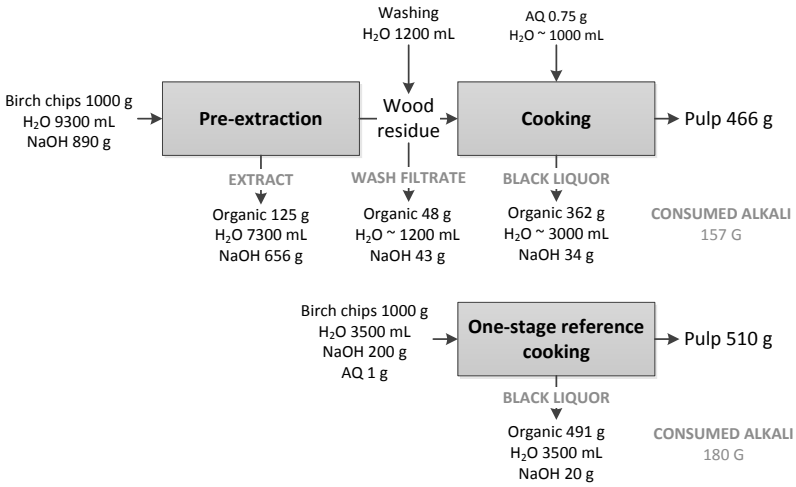

Figure 4.17. Mass balance of the organic phase and sodium hydroxide in pre-extraction pulping and reference SAQ pulping (based on paper IV).

The intrinsic viscosity of the pulps pre-treated with OA was, as expected, higher than that of the reference SAQ pulp (Table 4.5). An increase in the intrinsic viscosity is related to the removal of short-chain hemicelluloses. On the other hand, the somewhat lower intrinsic viscosity of the E-SAQ pulp indicated that a more severe hydrolytic degradation due to the higher alkali concentration pulping stage was involved.

Both pre-treatments – alkaline and acidic – allowed for shorter pulping durations to achieve target kappa numbers than in a reference cook (Table 4.7). In E-SAQ pulping the major reasons for the shorter pulping time are (a) better impregnation with alkali, (b) smaller amount of lignin-carbohydrate complexes due to the removal of xylan partly associated with the lignin, and (c) lower alkali consumption to neutralise carbohydrate degradation products. Prehydrolysis, on the other hand, is accompanied by lignin depolymerisation and breakage of lignin-carbohydrate complexes which facilitate the subsequent delignification in alkaline pulping (Schild et al., 1996, Rauhala et al., 2011). Prehydrolysis also facilitates wood impregnation in the pulping stage due to the formation of a more porous structure.

Some basic papermaking properties of the hemicellulose-lean paper pulps after oxygen delignification were compared to the reference values of an SAQ birch pulp. The studied pulps performed similarly in PFI mill refining (Table 4.8). The samples pre-treated with OA demonstrated a higher beating degree at the beginning of refining which could be attributed to a more disrupted fibre wall structure leading to higher water retention. The difference in the residual xylan content of 3.5% between E-SAQ and SAQ pulps had practically no effect on pulp beatability. A wet zero-span test was used to minimise the effect of fibre bonding on the strength of individual fibres (Table 4.8). The wet zero-span index indicated that the strength of the pre-treated fibres (0.120-0.127 kN•m/g) was

inferior to that of the reference fibres (0.141 kN•m/g). On the other hand, dry zero-span index measurement resulted in values for the pre-treated pulps closely resembling that of the reference. This result is supported by the observation of Gurnagul and Page (1989) that the strength of fibres may decrease upon rewetting. This observation was valid for pre-treated, bleached kraft, and unbleached sulphite pulps. It was suggested by Gurnagul and Page (1989) that changes in the composition of hemicellulose-lignin matrix in the fibre wall could weaken the wet fibres, allowing the fibrils to slide against one another. It can therefore be safely assumed that after alkaline and acidic pre-treatments, the reduction in the content of the hemicelluloses resulted in an inferior wet zero-span values of the fibres, though this does not affect the strength of dry fibres.

Table 4.8. Beating performance and some properties of the paper pulps (Paper IV, Testova et al. (2012a)).

	Beating energy, rev of PFI mill	Beating degree, °SR	App. density, kg/m3	Wet zero span index, kN*m/g	Dry zero span index, kN*m/g
SAQ	0	15.1	478	0.141	0.152
	1500	16.7	589		
	3000	19.8	624		
	5500	26.4	681		
P(OA)-SAQ	0	17.1	538	0.121	0.145
	1500	17.5	633		
	3000	20.0	655		
	5500	25.1	697		
P(OA)-SAQ-AQ	0	16.2	570	0.123	0.144
	1500	17.5	685		
	3000	19.5	711		
	5500	23.5	752		
P(OA)-SAQ-AQS	0	16.2	590	0.121	0.150
	1500	17.3	664		
	3000	19.5	707		
	5500	24.6	744		
P(OA)-SAQ-BH	0	15.5	527	0.127	0.155
	1500	16.6	609		
	3000	18.6	669		
	5500	23.5	702		
E-SAQ	0	15.2	456	0.120	0.151
	1500	16.7	553		
	3000	19.2	616		
	5500	26.1	665		

The apparent sheet density of the OA pre-treated pulps was slightly higher than for the SAQ and E-SAQ pulps, which may have been caused by denser packing of the more damaged fibres after acid prehydrolysis. The sheet strength properties are presented in Figure 4.18. At the bonding levels studied, the strength of fibre bonding plays a key role in the performance under tensile and tearing stress, meaning that the fibres tend to get pulled out of the network rather than breaking at the applied stress. Similarly to the studies by Schild et al. (2010) on eucalyptus and Testova (2006) on birch wood, here, OA prehydrolysis pulp (P(OA)-SAQ) without stabilisation exhibited tear and tensile strength indices inferior to those of the reference SAQ pulp. This result confirms the role of cellulose network integrity and hemicelluloses in papermaking. The tensile stiffness index also indicated that this pulp possessed the highest flexibility against the applied stress. Stabilisation of carbohydrates had a positive effect on the strength properties, due presumably to the higher xylan retention in pulp (Table 4.7). The stabilisation effect on the handsheet strength was particularly pronounced for the P(OA)-SAQ-BH pulp stabilised with BH. E-SAQ pulp exhibited excellent papermaking properties.

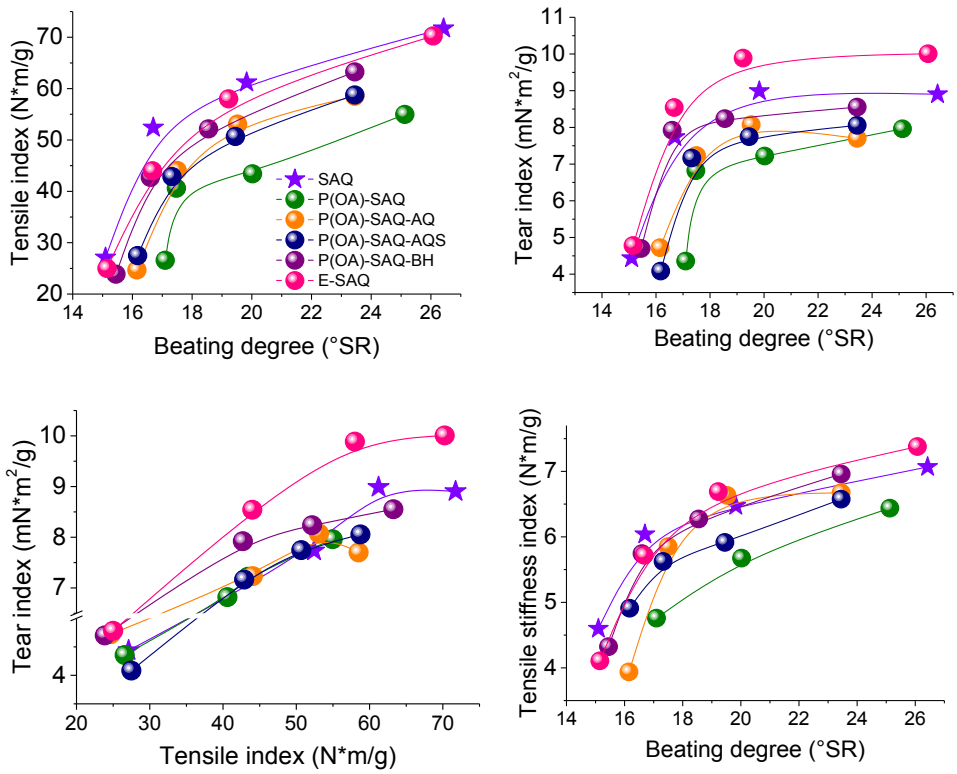

Figure 4.18. Papermaking properties of the pulps produced with alkaline and acidic pre-treatments (Testova et al., 2012b).

In addition to the papermaking properties studied, surface charge is a parameter responsible for interaction with papermaking additives and plays an important role in the performance of the fibres on a paper machine. The charge of the wood pulp fibres primarily originates from uronic acid substituents of xylan (Sjöström, 1989). Therefore, the effect of reduced xylan content in the pulp on the surface charge should be assessed in further studies.

4.5.4 Dissolving pulps (Paper III)

Dissolving pulps were produced under three prehydrolysis intensities (Tables 4.1 and 4.7). Higher prehydrolysis intensities ensured a more thorough removal of xylan not only during the prehydrolysis stage but also in pulping and bleaching operations. This behaviour can be attributed to better accessibility of xylan to chemicals and increased susceptibility towards alkaline degradation. The highest pulp purity was achieved in the case of P220 prehydrolysis with only 1.4% residual xylan content, which complies with a typical acetate-grade pulp specification. The pulp produced with the P170 prehydrolysis had a residual xylan content of 5.8% o.d. pulp, which is close to a viscose-grade pulp specification. Stabilisation of the carbohydrate fraction with borohydride (P170-S) allowed a 2% yield increase at the expense of pulp purity.

Cellulose degradation increased as a function of prehydrolysis intensity, as reflected in the decreased pulp intrinsic viscosity and the molar mass distributions shifted towards the smaller values, which is also reflected in a considerable decrease of the long-chain cellulose fraction (DP>2000) (Tables 4.7 and 4.9 and Figure 4.19). At the same time the low molar mass fraction of the P200 and P220 pulps (DP<100 fraction) decreased indicating a significant improvement of the purity. The alkali resistance (R18) of the P170 and P170-S samples exceeded measured cellulose content (Tables 4.7 and 4.9) due presumably to the alkali-stability of the hemicelluloses remaining in the pulps. On the other hand, pulps P200 and P220 contained highly-degraded cellulose which was reflected in the R18 values lower than expected according to cellulose content in the pulps. The subtraction of the R18 and R10 values indicated a high content of low molar mass cellulose in the P220 sample.

Table 4.9. Macromolecular properties and alkali resistances of bleached pulps (Paper III).

	P170	P170-S	P200	P220
Macromolecular properties				
Mn (kg/mol) [a]	76.9	72.0	75.5	58.6
Mw (kg/mol) [b]	352	330	245	175
PDI	4.6	4.6	3.2	2.9
DP<50	0.02	0.02	0.01	0.01
DP<100	0.04	0.05	0.03	0.04
DP<2000	0.61	0.63	0.74	0.81
DP>2000	0.33	0.30	0.22	0.14
Alkali resistance				
R18 (%)	95.8	95.5	94.0	96.5
R10 (%)	93.4	92.3	90.6	85.7
R18-R10 (%)	2.4	3.2	3.4	10.8

[a] number average molar mass
[b] weight average molar mass

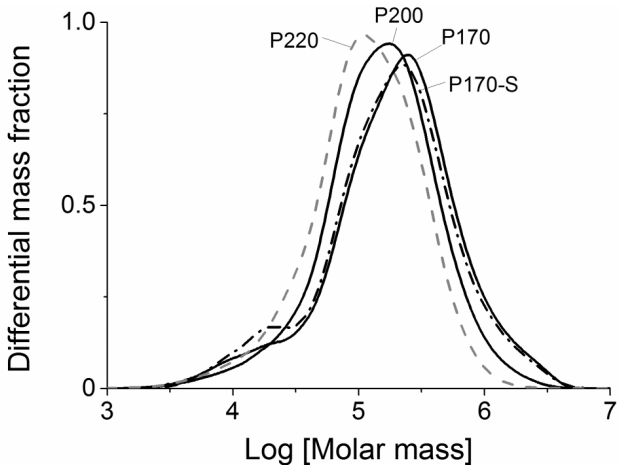

Figure 4.19. Molar mass distribution of dissolving pulps (Paper III).

The lateral dimensions measured using the wide-angle X-ray scattering technique (WAXS) and cross-polarisation magic angle spinning ^{13}C nuclear magnetic resonance spectroscopy (CP/MAS ^{13}C-NMR) were similar for all pulp samples (Table 4.10). The major difference in the crystal width was observed in the direction perpendicular to the (110) planes in WAXS analysis. Increased values were observed, presumably as a result of the aggregation in this direction or crystallisation of less ordered chains on the (110) or (1-10) surface when prehydrolysis was intensified. A decrease in the lateral fibril dimension at the highest prehydrolysis intensity observed by both WAXS and NMR likely originates from a disruption of cellulose chains on the microfibril surface. Cellulose crystallinity values obtained by WAXS and NMR were in good agreement and remained

practically unchanged with an increase in prehydrolysis intensity indicating that both amorphous and crystalline regions were degraded simultaneously (Table 4.10).

Table 4.10. Structural analysis of cellulose studied for bleached pulps (Paper III).

Sample				P170	P170-S	P200	P220
WAXS	Crystal width	nm	1-10	4.1	4.1	4.1	4.1
			110	3.4	3.3	4.4	4.1
			200	4.9	4.8	5.0	4.9
	Crystallinity	%		53 ± 3	54 ± 3	53 ± 3	54 ± 3
	Crystal length	nm		14.4 ± 1.0	14.0 ± 1.0	14.0 ± 1.0	14.0 ± 1.0
SAXS	Wet distance	nm		7.8 ± 0.1	7.6 ± 0.1	9.2 ± 0.1	9.4 ± 0.1
	Dry distance	nm		3.1 ± 0.2	3.1 ± 0.2	5.3 ± 0.2	5.5 ± 0.2
	Dry specific surface area	m^2/g		9.3	9.4	6.6	6.1
Solid state NMR	Crystallinity	%		53±1	52±1	53±1	55±1
	Lateral fibril dimension	nm		4.15±0.08	4.04±0.06	4.37±0.09	4.19±0.08
	Aggregate dimension	nm		22.5±0.6	20.7±0.5	21.1±0.6	18.7±0.6
	Wet specific surface area	m^2/g		118±3	129±3	127±4	143±5

The interfibrillar distances were determined by locating the scattering intensity peak maximums in small-angle X-ray scattering analysis (SAXS). The analysis demonstrated that smaller interfibrillar distances (3 nm) dominated in the samples prehydrolysed at 170 °C, while in the samples prehydrolysed under more severe conditions the dominant share of the microfibrils was located further apart from each other (6 nm). This behaviour may be explained by the disruption of the fibrillar structure, allowing microfibrils to drift apart after more severe prehydrolysis.

The specific surface area (SSA) values between microfibril aggregates were obtained by both SAXS and CP/MAS ^{13}C-NMR analyses in dry and rewetted state, respectively. The SSAs derived from SAXS analysis were larger in the samples P170 and P170-S (9.3-9.4 m^2/g) than in the samples P200 and P220 (6.1-6.6 m^2/g). The closure of the pores between the aggregates could be caused by the expansion of the individual aggregates as a result of increased distances between the microfibrils. Quite the opposite behaviour was observed in SSA values derived from NMR analysis. This phenomenon might be associated with the differences in the residual hemicellulose content of the samples. SAXS analysis revealed that upon rewetting the interfibrillar distance estimates increased by 150% for the hemicellulose-rich P170 and P170-S pulps, but only by 75% for the P200 and P220. It is suggested that hemicelluloses acting as spacers between microfibrils in the P170 and P170-S samples facilitated interfibrillar swelling in water. As a result the measured aggregate dimensions increased and the pore sizes decreased.

Application tests for the dissolving pulps included viscose filterability (Table 4.11) and laboratory triacetate properties (Table 4.12). The P170 sample with a residual xylan content of 5.8% demonstrated the best performance in viscose process simulation. The

viscose dope had a high filter value of F=417 and a low particle content of 12.1 ppm. A notable decrease in the dope quality was observed for the P170-S sample as a result of its higher xylan content, which hindered alkali penetration to the fibre wall. The filter value for the P170-S pulp decreased to F=332, corresponding to faster filter clogging. The P200 sample having higher purity than a typical viscose grade pulp (2.8%), was not suitable for viscose production. The filterability of the dope was rather poor (F = 218), and the particle content of 98.3 ppm was unacceptably high. The poor performance of the P200 pulp in viscose process simulation is probably attributed mainly to structural changes such as increased crystal width and small specific surface area that may hinder cellulose accessibility to the reagents. Due to the high purity of the P220 pulp, it was not considered as a potential viscose grade pulp.

Table 4.11. Viscose filterability (Paper III).

Sample	Viscose filterability		
	Filter value (F)	Particle content (P)	Quality allocation
		ppm	
P170	417	12.1	Good
P170-S	332	12.1	satisfactory
P200	218	98.3	poor
P220	n.d.	n.d.	
Viscose grade pulp [a]	400-600	5-10	

[a] Commercial PHK hardwood pulp

n.d. not determined

All four dissolving pulps were used to produce cellulose triacetates on a laboratory scale. The reaction time required to complete acetylation is closely associated with the reaction rate and was the greatest for the P170 and P170-S pulps (95 min) (Table 4.12). The P200 pulp demonstrated optimal reactivity in the selected conditions with only 22 minutes required to complete acetylation. This result was in line with that of the commercial hardwood acetate grade pulp. Due to a low DP, the P220 sample was highly reactive in such a manner that it was not possible to control reliably the reaction completion. A more controlled acetylation process would require adjustment of the reaction recipe. Optical properties of the obtained triacetate dopes were evaluated by measuring yellowness and clarity (transmittance). Both values were found to be directly related to the residual xylan content in the pulps, which is known to impart haze and yellowness to the dope. The clarity values of the P200 and P220 triacetate acetate dopes (79.8% and 81.1%) were comparable to those of the highest purity plastic grade commercial hardwood pulp (82.0%) (Table 4.12). The yellowness of the purest P220 sample was sufficiently low (0.24) to meet the specification requirements for the filter tow quality (0.23). High yellowness could have been caused by the higher content of inorganic compounds in the laboratory samples.

Table 4.12. Cellulose triacetate properties (Paper III).

Sample	Xylan content	Acetylation time	Ball fall viscosity	Transmittance	Yellowness
	% o.d. wood	min	s	%	
P170	5.8	95	35	74.1	0.54
P170-S	7.2	95	35	69.3	0.63
P200	2.8	22	33	79.8	0.35
P220	1.4	18	17	81.1	0.24
Viscose pulp [a]	2.8	40	22	77	0.38
Acetate pulp, filter tow grade [a]	1.8	68	33	83	0.23
Acetate pulp, plastic grade [a]	1.2	30	25	82	0.15

[a] Commercial PHK hardwood pulps

4.6 Economic considerations

The material and energy balance of pulp production are strongly affected by pre-treatment (Tables 4.13 and 4.14). Isolation of the organic matter, which would typically be found in the spent pulping liquor, could potentially debottleneck the recovery boiler and allow for increased pulp production. This is particularly important when steam prehydrolysis is replaced by an aqueous-phase prehydrolysis for a dissolving pulp production. However, this is achievable only when sufficiently large amounts of the released carbohydrate degradation products can be separated from the hydrolysate in practice. As demonstrated in Tables 4.13 and 4.14, in all prehydrolysis scenarios the content of the dissolved organic solids in the black liquor per tonne of produced pulp exceeded that of the reference SAQ pulp. This is attributed to (a) low recovery of the prehydrolysates from the wood residue, and (b) more extensive degradation of the wood residue during pulping than in the reference SAQ case. Introducing a pre-treatment to a paper-grade pulp production line will likely be associated with a reduced pulp yield (Table 4.13) and intensification of prehydrolysis in the dissolving pulp production will produce pulps with very low yields (Table 4.14). If the wood intake is maintained at the same level as before the process modification, pulp output will be decreased and energy production from black liquor may also decrease (Table 4.13 and 4.14). In order to maintain the target pulp output at the reference level, a higher wood intake has to be considered (Table 4.13 and 4.14). In that case, the organic load of the black liquor may significantly exceed the reference level. Sufficient capacity of both the fibreline and the energy recovery cycle should, therefore, be ensured. Another energy-related consideration is reduced concentration of the black liquor dissolved solids: in the experiments performed the liquid-to-solid ratio maintained a constant 3.5 L/kg initial

wood (Tables 4.13 and 4.14). The liquid-to-solid ratio of the pulping stage should, therefore, be carefully adjusted to minimise the steam demand for evaporation of the black liquor.

The separation efficiency of a prehydrolysate or a pre-extract from the wood residue also directly affects the yield of the dissolved hemicelluloses and the amount of acid/alkali remaining in the wood residue for the pulping stage. Only moderate amounts of xylan can be recovered by simple discharge of the liquid phase (Tables 4.13 and 4.14). An intermediate washing step should be avoided on a commercial scale due to the high cost, so a more thorough drainage of the liquid phase needs to be realised in practice.

The economic feasibility of the modified pulping processes depends heavily on the revenue from the products derived from hemicelluloses. At the moment, XOS appear to have the highest value added among commercial xylan-derived products. Birch wood prehydrolysates, particularly after autohydrolysis in mild conditions, are rich in XOS (Table 4.13). However, the presence of monomeric xylose and its degradation products complicates separation and purification. Prehydrolysates produced under more severe conditions or in the presence of acids contain substantial amounts of monomeric xylose (Tables 4.13 and 4.14). Isolated xylose can be used as is or converted to xylitol, furfural, or building block chemicals. When xylan is isolated in polymeric form by alkaline pre-extraction (Table 4.13), enzymatic hydrolysis can selectively produce XOS with minimal contamination by xylose. Alternatively, functionalised xylan can be converted into materials or used as is as a papermaking additive. While acetic acid is an additional product of prehydrolysis process, in alkaline pre-extraction cleaved acetyl groups are converted to sodium acetate and cannot be recovered in a commercially viable way. However, to ensure feasible production of various xylan derivatives, commercially attractive separation, purification, and conversion methods should be developed.

Utilisation of chemicals and enzymes in different process stages should be carefully considered. Alkaline pre-extraction requires a substantial alkali charge several times greater than that of an alkaline pulping (Table 4.13), while the consumption of alkali is lower than in the reference SAQ process. Recirculation of the recovered unconsumed alkali to pre-extraction and other process stages determines the process feasibility. In prehydrolysis the use of acid reduces the steam demand for heating and creates an additional cost for the acid. Additionally, OA, which was a subject of this study, easily forms insoluble oxalates that may lead to scaling problems in the process equipment (Häärä et al., 2011). The limited solubility of most of the oxalates in water can also be used for separation and regeneration purposes. Application of AQ and its derivatives for pulping purposes may be limited due to the potential carcinogenic danger. High price, toxicity and formation of hydrogen upon decomposition of BH will likely prevent its applicability on an industrial scale. Thus, seeking alternative stabilisation methods might also be considered.

Implementing a pre-treatment stage in an existing pulp mill requires major investments. The shorter pulping duration achievable after a pre-treatment may allow retrofitting an existing impregnation vessel, if available, for pre-treatment. Separation and purification of the isolated hemicelluloses as well as conversion to marketable products make the process very cost intensive; however, valorisation of the extracted organic fractions is a prerequisite for cost effectiveness.

Table 4.13. Product specification and energy output of the combined production of xylan and paper pulps.

	SAQ	P(OA)-SAQ	P(OA)-SAQB	E-SAQ
Isolated xylan				
Yield[1], % o.d. wood		2.8		6.6
Solubility		Water soluble		Alkali soluble, water insoluble
Macromolecular properties		Mono- and oligomers (proportion 1:1)		Polymeric 20 kg/mol
Side chains		In oligomers acetyl and MeGlcA		MeGlcA, HexA
Impurities		Lignin 1.5 % o.d. wood, other carbohydrates, extractives, furanic compounds, organic acids		Lignin 1.1% o.d. wood, other carbohydrates, extractives, salts of organic acids, NaOH
Paper pulps (after oxygen delignification)				
Yield, % o.d. wood	49.6	41.9	46.0	44.7
Xylan content, % pulp	12.5	6.1	8.0	9.0
Intrinsic viscosity, mL/g	945	1147	1104	878
Kappa number	13.1	12.9	9.0	12.1
Papermaking properties	Reference	Inferior to reference	Close to reference	The same as reference
Distribution of the dry solids based on 1 tonne of produced pulp (t) [2]				
Wood intake for 1 t of pulp	2.0	2.4	2.2	2.2
Solids in the pre-treatment liquid phase		0.13	0.11	0.39
Solids in the black liquor	1.0	1.26	1.06	0.85
Concentration of solids in the BL, kg/m³	*140*	*151*	*139*	*103*
Pulp output	1.0	1.0	1.0	1.0
Xylan output		0.067	0.062	0.15
NaOH charge	0.40	0.48	0.44	2.0
NaOH consumption	0.36	0.43	0.40	0.35
Oxalic acid charge		0.043	0.040	
Heat value of black liquors, GJ/t	*19.6*	*20.6*	*21.2*	*21.2*
Energy generation, GJ	*19.9*	*25.9*	*22.5*	*18.1*

[1] Minimal yield achievable after draining the hydrolysate from the solid phase in laboratory conditions without applying washing (P(OA)) or after one washing stage (E).
[2] The distribution of dry solids based on 1 t of wood intake can be calculated by dividing the values in the table by the wood intake for 1 t of pulp.
HexA – hexenuronic acids

Table 4.14. Product specification and energy output of the combined production of xylan and dissolving pulps.

	PHK Viscose	PHK acetate	P170-SAQ	P200-SAQ	P220-SAQ
Isolated xylan					
Yield[1]			9.9	6.3[2]	5.7[2]
Solubility			Water soluble		
Macromolecular properties			Mono- and oligomers (proportion 9:10)	Mono- and oligomers (proportion 9.2:10)	Mono- and oligomers (proportion 13:10)
Side chains			In oligomers acetyl groups and MeGlcA		
Impurities			Lignin, other carbohydrates, furanic compounds, organic acids, extractives		
Bleached dissolving pulps					
Yield, % o.d. wood	35	30	34.1	30.3	22.9
Xylan content, % pulp	2.8	1.8	5.8	2.8	1.4
Cellulose content, % pulp	97.2	98.0	94.2	97.2	98.6
Intrinsic viscosity, mL/g	468	585	507	432	307
Performance as viscose grade	Reference		Good	Poor	Not tested
Performance as acetate grade		Reference	Poor optical properties	Similar to PHK viscose	Good, but low viscosity
Distribution of dry solids based on 1 tonne of produced pulp (t) [3]					
Wood intake for 1 t of pulp			2.9	3.3	4.4
Solids in the pre-treatment liquid phase			0.45	0.84	1.44
Solids in the black liquor (BL)			1.18	1.19	1.63
Concentration of solids in the BL, kg/m3			*144*	*126*	*126*
Pulp output			1.0	1.0	1.0
Xylan output			0.29	0.21	0.25
NaOH charge			0.64	0.73	0.97
NaOH consumption			0.44	0.46	0.57
Heat value of black liquors, GJ/t			*21.4*	*21.2*	*20.7*
Energy generation, GJ			*31.6*	*31.0*	*40.0*

[1] Minimal yield achievable after draining the hydrolysate from the solid phase in laboratory conditions without applying washing.
[2] Recovery of degradation products like furfural may be considered.
[3] The distribution of dry solids based on 1 t of wood intake can be calculated by dividing the values in the table by the wood intake for 1 t of pulp.

5. Concluding remarks

Isolation of wood hemicelluloses as a raw material for value-added products is one of the principal focus areas in biorefinery. In the present work, different aspects of the isolation of xylan from birch wood were investigated. Acidic prehydrolysis and alkaline pre-extraction in connection with alkaline pulping were in the study's spotlight.

A mass balance of birch autohydrolysis at two process intensities was completed. A special emphasis was placed on the properties of xylan in the liquid phase and the solid residue. The distribution of the xylan with its substituents was monitored in both the liquid and solid phases with a special emphasis on XOS formation in the prehydrolysates. When acid-catalysed prehydrolysis was compared with autohydrolysis, a major difference in the product composition was noted. Oxalic acid-aided process facilitated hydrolysis to monomeric xylose yielding prehydrolysates with a more homogeneous composition than in autohydrolysis. This study can serve as a tool to predict and adjust the composition of wood prehydrolysates.

The impact of the newly-formed cellulose reducing ends in prehydrolysis conditions on the subsequent alkaline degradation of cellulose was studied with special attention. A study on a model cellulose substrate – cotton linters – was performed to investigate this phenomenon. Oxidative and reductive additives capable of converting cellulose REGs to the functionalities stable against alkaline peeling were evaluated. Stabilisation of cellulose was evident through the increased yield after alkaline degradation with the in-situ addition of stabilisation chemicals. The results were also supported by the balance of functionalities at the reducing ends which confirmed the stabilisation mechanism. The model study provided further insight into the role of the reducing end functionalities in preserving cellulose yield.

An improved model of cellulose degradation in alkaline environments was developed by taking secondary peeling into account. The degradation data produced a good fit with the improved model. The alkaline hydrolysis rate constants were found to be two orders of magnitude smaller than those calculated with the conventional model. The validity of the findings was confirmed by evaluating the first-order kinetics of cellulose chain scission which is closely related to alkaline hydrolysis.

The knowledge gained about prehydrolysis was applied to produce dissolving pulps by a combination of autohydrolysis and alkaline pulping without a subsequent alkaline post-extraction. A wide range of prehydrolysis intensities allowed production of both viscose- and acetate-grade pulps of high quality and performance in application tests. Pre-treated pulps also showed potential for papermaking. Excellent extraction results were achieved with an alkaline pre-extraction process that selectively isolated polymeric xylan while preserving cellulose properties. The isolated xylan is deemed to be a good candidate for the production of XOS and materials. Pre-extraction pulping yielded fibres with strength properties highly competitive with those of the reference pulp. Oxalic acid prehydrolysis pulps with somewhat inferior papermaking properties could find applications for paper specifications with lower strength requirements.

When stabilisation of the reducing end-groups was applied to prehydrolysed wood, a very low efficiency of cellulose stabilisation was observed. Limited cellulose accessibility to the stabilisation additives and the competing reactions with the hemicelluloses affected stabilisation. An attempt to increase the yield of the viscose grade pulp by in-situ addition of BH resulted in a pulp with an increased xylan content, which had a negative impact on the viscose filterability. The major positive effect of the stabilisation was observed in the production of prehydrolysis paper pulps. Papermaking properties were enhanced to a level close to that of the reference SAQ pulp, due apparently to an increase in the residual hemicelluloses content. The non-selective mechanism of carbohydrate stabilisation in wood is a matter of consideration when selecting a pulping protocol for a given pulp grade.

The work conducted contributed to the existing knowledge of wood fractionation on both the fundamental and applied levels. The evaluation performed of the isolated xylan properties as a function of pre-treatment conditions can be used for designing potential products. The possibility of producing high quality pulps and value-added hemicellulose-based products is a key factor for industrial realisation. New insights on the role of the reducing ends in the behaviour of polysaccharides can find further development on a broader scale than biomass fractionation. Finally, as a result of this work, the high potential of birch wood biorefinery was spotlighted.

6. Future work and outlook

Recent years have witnessed the first steps towards a bio-based economy. However, robust systems based on innovative and cost-efficient use of lignocellulosic materials in highly integrated biorefinery facilities are required to ensure competitiveness and stability in the long run. To realise this ambition, research efforts in the field of biorefineries should not only focus on the fundamental principles, but also on the possibilities of bringing the concept of biorefinery closer to commercial realisation.

Alkaline pre-extraction has demonstrated a high economic potential for the combined production of paper-grade pulps and polymeric hardwood xylan. A detailed feasibility study of the concept and scale-up tests should determine the actual implementation perspectives of the process at an industrial scale. The principal questions related to the pre-extraction process which require further examination are:

(a) efficient separation of the extract from the solid phase to maintain appropriate alkali charge for the subsequent pulping process while avoiding washing steps;
(b) economically feasible concentration of the extracts by filtration, ensuring a high service life of the costly membranes;
(c) complete recycling of the concentrated and diluted alkali fractions into the process steps;
(d) finding commercial value-added applications of the polymeric isolated xylan.

Aqueous-phase prehydrolysis has already been applied on an industrial scale. However, technically and commercially attractive ways to purify and valorise the extracted carbohydrates and acetic acid are still missing. The challenges related to the utilisation of the prehydrolysates involve:

(a) efficient and commercially attractive removal of sticky lignin products from the hydrolysate;
(b) high heterogeneity of the mixtures and the lack of commercially available processes to fractionate the individual components and remove inhibitors;
(c) in the case of flow-through systems that allow the production of prehydrolysates in a narrow range of molar masses, generation of large volumes of diluted prehydrolysates is problematic;
(d) a lack of highly selective and efficient methods to convert C_5 sugars into products.

Furthermore, introducing prehydrolysis prior to the pulping stage is associated with reduced pulp yields and alteration of fibre papermaking properties in the case of paper-grade pulps and a very low degree of polymerisation in the case of extremely pure dissolving pulps.

To summarise, for both alkaline pre-extraction and prehydrolysis, future work has to focus primarily on innovative processes enabling efficient handling and valorisation of the received xylan fractions.

References

Aachary, A.A., Prapulla, S.G., (2011). Xylooligosaccharides (XOS) as an emerging prebiotic: Microbial synthesis, utilization, structural characterization, bioactive properties, and applications. Comprehensive Reviews in Food Science and Food Safety. 10, 2-16.

Al-Dajani, W.W., Tschirner, U.W., (2008). Pre-extraction of hemicelluloses and subsequent kraft pulping. Part I: alkaline extraction. Tappi Journal. 7, 3-8.

Al-Dajani, W.W., Tschirner, U.W., Jensen, T., (2009). Pre-extraction of hemicelluloses and subsequent kraft pulping. Part II: acid- and autohydrolysis. Tappi Journal. 8, 30-37.

Al-Dajani, W.W., Tschirner, U.W., (2010). Pre-extraction of hemicelluloses and subsequent ASA and ASAM pulping: comparison of autohydrolysis and alkaline extraction. Holzforschung. 64, 411-416.

Alekhina, M., Mikkonen, K.S., Alen, R., Tenkanen, M., Sixta, H., (2014). Carboxymethylation of alkali extracted xylan for preparation of bio-based packaging films. Carbohydrate Polymers. 100, 89-96.

Alen, R., (2000a). Structure and chemical composition of wood. in: R. Alens, Forest products chemistry. Finnish Paper Engineers' Association, Helsinki, pp. 11-57.

Alen, R., (2000b). Basic chemistry of wood delignification. in: R. Alens, Forest products chemistry. Finnish Paper Engineers' Association, Helsinki, pp. 58-104.

Andersson, C., Hodge, D., Berglund, K.A., Rova, U., (2007). Effect of different carbon sources on the production of succinic acid using metabolically engineered Escherichia coli. Biotechnology Progress. 23, 381-388.

Andritz, ANDRITZ pre-hydrolysis cooking for dissolving pulp production. Retrieved from, http://www.andritz.com/products-and-services/pf-detail.htm?productid=15087.

Berggren, R., Berthold, F., Sjoholm, E., Lindstrom, M., (2003). Improved methods for evaluating the molar mass distributions of cellulose in kraft pulp. Journal of Applied Polymer Science. 88, 1170-1179.

Bernardin, L.J., (1958). The nature of the polysaccharide hydrolysis in black gumwood treated with water at 160°. Tappi. 41, 491-499.

Bernstein, L., Bosch, P., Canziani, O., Chen, Z., Christ, R., Davidson, O., Hare, W., Huq, S., Karoly, D., Kattsov, V., Kundzewicz, Z., Liu, J., Lohmann, U., Manning, M., Matsuno, T., Menne, B., Metz, B., Mirza, M., Nicholls, N., Nurse, L., Pachauri, R., Palutikof, J., Parry, M., Qin, D., Ravindranath, N., Reisinger, A., Ren, J., Riahi, K., Rosenzweig, C., Rusticucci, M., Schneider, S., Sokona, Y., Solomon, S., Stott, P., Stouffer, R., Sugiyama, T., Swart, R., Tirpak, D., Vogel, C., Yohe, G., (2007). Climate change 2007: Synthesis report. An Assessment of the Intergovernmental Panel on Climate Change. http://www.ipcc.ch/pdf/assessment-report/ar4/syr/ar4_syr.pdf.

Bfr Federal Institute for Risk Assessment, (2013). BfR removes anthraquinone from its list of recommendations for food packaging. BfR opinion No. 005/2013.

Blain, T.J., (1993). Anthraquinone pulping: fifteen years later. Tappi Journal. 76, 137-146.

Bobleter, O., (1994). Hydrothermal degradation of polymers derived from plants. Progress in Polymer Science. 19, 797-841.
Bobleter, O., (2004). Hydrothermal degradation and fractionation of saccharides and polysaccharides (Fortsetzung). in: S. Dumitrius, Polysaccharides. structural diversity and functional versatility, second edition. Marcel Dekker, New York, pp. 804-834.
Borrega, M., Nieminen, K., Sixta, H., (2011a). Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures. Bioresource Technology. 102, 10724-10732.
Borrega, M., Nieminen, K., Sixta, H., (2011b). Effects of hot water extraction in a batch reactor on the delignification of birch wood. BioResources. 6, 1890-1903.
Borrega, M., Sixta, H., (2013). Purification of cellulosic pulp by hot water extraction. Cellulose. 20, 2803-2812.
Borrega, M., Tolonen, L.K., Bardot, F., Testova, L., Sixta, H., (2013a). Potential of hot water extraction of birch wood to produce high-purity dissolving pulp after alkaline pulping. Bioresource Technology. 135, 665-671.
Borrega, M., Niemelä, K., Sixta, H., (2013b). Effect of hydrothermal treatment intensity on the formation of degradation products from birchwood. Holzforschung. 67, 871-879.
Borregaard.Com, http://www.borregaard.com/.
Bose, S.K., Omori, S., Kanungo, D., Francis, R.C., Shin, N.H., (2009). Mechanistic differences between kraft and soda/AQ pulping. Part 1: Results from wood chips and pulps. Journal of Wood Chemistry and Technology. 29, 214-226.
Bozell, J.J., (2010). Connecting biomass and petroleum processing with a chemical bridge. Science. 329, 522-523.
Brandt, A., Grasvik, J., Hallett, J.P., Welton, T., (2013). Deconstruction of lignocellulosic biomass with ionic liquids. Green Chemistry. 15, 550-583.
Brasch, B.J., Free, K.W., (1965). Prehydrolysis-kraft pulping of Pinus radiata grown in New Zealand. Tappi. 48, 245-248.
Carvalho, A.F.A., De, O.N.P., Fernandes, D.S.D., Pastore, G.M., (2013). Xylo-oligosaccharides from lignocellulosic materials: Chemical structure, health benefits and production by chemical and enzymatic hydrolysis. Food Research International. 51, 75-85.
Chen, X., Lawoko, M., Heiningen, A.V., (2010). Kinetics and mechanism of autohydrolysis of hardwoods. Bioresource Technology. 101, 7812-7819.
Cherubini, F., Jungmeier, G., Wellisch, M., Willke, T., Skiadas, I., Van Ree, R., De Jong, E., (2009). Toward a common classification approach for biorefinery systems. Biofuels, Bioproducts and Biorefining. 3, 534-546.
Christopher, L.P., (2013). Integrated forest biorefineries: current state and development potential. RSC Green Chemistry Series. 18, 1-66.
Christov, L.P., Prior, B.A., (1993). Xylan removal from dissolving pulp using enzymes of Aureobasidium pullulans. Biotechnology Letters. 15, 1269-1274.
Chunilall, V., Bush, T., Larsson, P.T., Iversen, T., Kindness, A., (2010). A CP/MAS 13C-NMR study of cellulose fibril aggregation in eucalyptus dissolving pulps during drying and the correlation between aggregate dimensions and chemical reactivity. Holzforschung. 64, 693-698.
Clark, J.H., Budarin, V., Deswarte, F.E.I., Hardy, J.J.E., Kerton, F.M., Hunt, A.J., Luque, R., Macquarrie, D.J., Milkowski, K., Rodriguez, A., Samuel, O., Tavener, S.J., White, R.J., Wilson, A.J., (2006). Green chemistry and the biorefinery: a partnership for a sustainable future. Green Chemistry. 8, 853-860.
Clark, J.H., Luque, R., Matharu, A.S., (2012). Green chemistry, biofuels, and biorefinery. Annual Review of Chemical and Biomolecular Engineering. 3, 183-207.
Clayton, D.W., Marraccini, L.M., (1966). The effect of additives on the stability of polysaccharides in hot alkali. Svensk Papperstidning. 69, 311-321.

Conner, A.H., (1984). Kinetic modeling of hardwood prehydrolysis. Part I. Xylan removal by water prehydrolysis. Wood and Fiber Science. 16, 268-277.
Copur, Y., Tozluoglu, A., (2008). A comparison of kraft, PS, kraft-AQ and kraft-NaBH4 pulps of Brutia pine. Bioresource Technology. 99, 909-913.
Costabel, L. (2013). Alkaline pre-extraction of birch wood prior to alkaline pulping. *Department of Forest Products Technology*. Aalto University, Montevideo.
Dahl, O., Martikka, M., Watkins, G., (2008). Environmental management and control. Finnish Paper Engineers' Association, Helsinki, 304 pp.
Davidson, G.F., (1948). Acidic properties of cotton cellulose and derived oxy-celluloses. II. Absorption of methylene blue. Journal of the Textle Institute. 39, T65-86.
De Lopez, S., Tissot, M., Delmas, M., (1996). Integrated cereal straw valorization by an alkaline pre-extraction of hemicellulose prior to soda-anthraquinone pulping. Case study of barley straw. Biomass Bioenergy. 10, 201-211.
Demirbas, M.F., (2009). Biorefineries for biofuel upgrading: A critical review. Applied Energy. 86, Supplement 1, S151-S161.
Deutschmann, R., Dekker, R.F.H., (2012). From plant biomass to bio-based chemicals: Latest developments in xylan research. Biotechnology Advances. 30, 1627-1640.
Di Nicola, G., Santecchia, E., Santori, G., Polonara, F., (2011). Advances in the development of bioethanol: a review. in: M.a.D.S. Bernardess, Biofuel's engineering process technology. Available from: http://www.intechopen.com/books/biofuel-s-engineering-process-technology/advances-in-the-development-of-bioethanol-a-review, pp. 611-638.
Dodds, D.R., Gross, R.A., (2007). Chemicals from biomass. Science. 318, 1250-1251.
Domsjo.Adityabirla.Com, http://www.domsjo.adityabirla.com/.
Dudkin, M.S., Gromov, V.S., Vedernikov, N.A., Katkevich, R.G., Cherno, N.K., (1991). Hemicelluloses. Zinatne, Riga, 488 pp.
Ebringerova, A., Hromadkova, Z., Heinze, T., (2005). Hemicellulose. Advances in Polymer Science. 186, 1-67.
Engelberth, A.S., Van Walsum, G.P., (2012). Adding value to the integrated forest biorefinery with co-products from hemicellulose-rich pre-pulping extract. in: C. Bergeron, D.J. Carrier,S. Ramaswamys, Biorefinery co-products: phytochemicals, primary metabolites and value-added biomass processing. John Wiley & Sons Ltd., Noida, pp. 287-310.
Escalante, A., Gonçalves, A., Bodin, A., Stepan, A., Sandström, C., Toriz, G., Gatenholm, P., (2012). Flexible oxygen barrier films from spruce xylan. Carbohydrate Polymers. 87, 2381-2387.
Evstigneev, E.I., Shalimova, T.V., (1985). Redox properties, catalytic activity, and stabilizing effect of some quinones during soda pulping. 2. Effect on pulping. Khimiya Drevesiny. 55-60.
Fang, J.M., Sun, R.C., Salisbury, D., Fowler, P., Tomkinson, J., (1999). Comparative study of hemicelluloses from wheat straw by alkali and hydrogen peroxide extractions. Polymer Degradation and Stability. 66, 423-432.
Fasching, M., Kandioller, G., Griebl, A., Weber, H., Sixta, H. (2006). Multistage sulfite pulping studied by lignin model reactions. *European Workshop on Lignocellulosics and Pulp*. Vienna.
Fatehi, P., Ni, Y., (2011a). Integrated forest biorefinery - sulfite process. ACS Symposiun Series. 1067, 409-441.
Fatehi, P., Ni, Y., (2011b). Integrated forest biorefinery - prehydrolysis/dissolving pulping process. ACS Symposiun Series. 1067, 475-506.
Fengel, D., Wegener, G., (1984). Wood: Chemistry, Ultrastructure, Reactions. Walter de Gtuyter, Berlin, 613 pp.
Fitzpatrick, M., Champagne, P., Cunningham, M.F., Whitney, R.A., (2010). A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products. Bioresource Technology. 101, 8915-8922.

Fleming, B.I., Kubes, G.J., Macleod, J.M., Bolker, H.I., (1978). Soda pulping with anthraquinone. Tappi. 61, 43-46.
Francis, R.C., Bolton, T.S., Abdoulmoumine, N., Lavrykova, N., Bose, S.K., (2008). Positive and negative aspects of soda/anthraquinone pulping of hardwoods. Bioresource Technology. 99, 8453-8457.
Froschauer, C., Hummel, M., Iakovlev, M., Roselli, A., Schottenberger, H., Sixta, H., (2013). Separation of hemicellulose and cellulose from wood pulp by means of ionic liquid/cosolvent systems. Biomacromolecules. 14, 1741-1750.
Fuhrmann, A., Krogerus, B. (2009). Xylan from bleached hardwood pulp – new opportunities. *TAPPI engineering, pulping & environmental conference*. pp. 2668-2675. Memphis, TN, USA.
Garcia, E., Johnston, D., Whitaker, J.R., Shoemaker, S.P., (1993). Assessment of endo-1,4-beta-D-glucanase activity by a rapid colorimetric assay using disodium 2,2'-bicinchoninate. Journal of Food Biochemistry. 17, 135-145.
Garrote, G., Dominguez, H., Parajó, J.C., (1999a). Hydrothermal processing of lignocellulosic materials. Holz als Roh- und Werkstoff. 57, 191-202.
Garrote, G., Dominguez, H., Parajo, J.C., (1999b). Mild autohydrolysis: an environmentally friendly technology for xylooligosaccharide production from wood. Journal of Chemical Technology and Biotechnology. 74, 1101-1109.
Garrote, G., Kabel, M.A., Schols, H.A., Falqué, E., Domínguez, H., Parajó, J.C., (2007). Effects of Eucalyptus globulus wood autohydrolysis conditions on the reaction products. Journal of Agricultural and Food Chemistry. 55, 9006-9013.
Gehmayr, V., Schild, G., Sixta, H., (2011). A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application. Cellulose. 18, 479-491.
Gehmayr, V., Sixta, H., (2012). Pulp Properties and Their Influence on Enzymatic Degradability. Biomacromolecules. 13, 645-651.
Gibson, G.R., Roberfroid, M.B., (1995). Dietary modulation of the human colonic microbiota: Introducing the concept of prebiotics. The Journal of Nutrition. 125, 1401-1412.
Gravitis, J., Abolins, J., (2013). Biorefinery technologies for biomass conversion into chemicals and fuels towards zero emissions (Review). Latvian Journal of Physics and Technical Sciences. 50, 29-43.
Griebl, A., Lange, T., Weber, H., Milacher, W., Sixta, H., (2005). Xylo-oligosaccharide (XOS) formation through hydrothermolysis of xylan derived from viscose process. Macromolecular Symposia. 232, 107-120.
Gröndahl, M., Eriksson, L., Gatenholm, P., (2004). Material Properties of Plasticized Hardwood Xylans for Potential Application as Oxygen Barrier Films. Biomacromolecules. 5, 1528-1535.
Gubitz, G.M., Stebbing, D.W., Johansson, C.I., Saddler, J.N., (1998). Lignin-hemicellulose complexes restrict enzymic solubilization of mannan and xylan from dissolving pulp. Applied Microbiology and Biotechnology. 50, 390-395.
Gullon, P., Gonzalez-Munoz, M.J., Van Gool, M.P., Schols, H.A., Hirsch, J., Ebringerova, A., Parajo, J.C., (2010). Production, refining, structural characterization and fermentability of rice husk xylooligosaccharides. Journal of Agricultural and Food Chemistry. 58, 3632-3641.
Gurnagul, N., Page, D.H., (1989). The difference between dry and rewetted zero-span tensile strength of paper. Tappi Journal. 72, 164-167.
Gübitz, G.M., Lischnig, T., Stebbing, D., Saddler, J.N., (1997). Enzymatic removal of hemicellulose from dissolving pulps. Biotechnology Letters. 19, 491-495.
Gütsch, J.S., Sixta, H., (2011). The HiTAC-process (high temperature adsorption on activated charcoal) - new possibilities in autohydrolysate treatment. Lenzinger Berichte. 89, 142-151.
Gütsch, J.S., Nousiainen, T., Sixta, H., (2012). Comparative evaluation of autohydrolysis and acid-catalyzed hydrolysis of Eucalyptus globulus wood. Bioresource Technology. 109, 77-85.

Haas, D.W., Hrutfiord, B.F., Sarkanen, K.V., (1967). Kinetic study on the alkaline degradation of cotton hydrocellulose. Journal of Applied Polymer Science. 11, 587-600.
Hakala, T.K., Liitiä, T., Suurnäkki, A., (2013). Enzyme-aided alkaline extraction of oligosaccharides and polymeric xylan from hardwood kraft pulp. Carbohydrate polymers. 93, 102-108.
Hamilton, J.K., Quimby, G.R., (1957). The extractive power of lithium, sodium, and potassium hydroxide solutions for the hemicelluloses associated with wood cellulose and holocellulose from western hemlock. Tappi. 40, 781-786.
Heikkilä, H., Lindroos, M., Sundquist, J., Kauliomäki, S., Rasimus, R., (2004). Preparation of chemical pulp and xylose, utilizing a direct acid hydrolysis on the pulp. US Patent 6(752):902.
Heikkilä, H., Hyöky, G., Rahkila, L., Sarkki, M.L., Viljava, T., (2005). Process for the simultaneous production of xylitol and ethanol. US Patent 6846657 B2.
Helmerius, J. (2010). Integration of a hemicelluloses extraction step into a forest biorefinery for production of green chemicals. *Department of Civil, Environmental and Natural Resources Engineering*. Luleå University of Technology, Luleå.
Helmerius, J., Von Walter, J.V., Rova, U., Berglund, K.A., Hodge, D.B., (2010). Impact of hemicellulose pre-extraction for bioconversion on birch Kraft pulp properties. Bioresource Technology. 101, 5996-6005.
Hoydonckx, H.E., Van Rhijn, W.M., Van Rhijn, W., De Vos, D.E., Jacobs, P.A., (2000). Furfural and derivatives. in: Wiley-Vchs, Ullmann's encyclopedia of industrial chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, Published online, pp. 285-313.
Huang, H.-J., Ramaswamy, S., Al-Dajani, W.W., Tschirner, U., (2010). Process modeling and analysis of pulp mill-based integrated biorefinery with hemicellulose pre-extraction for ethanol production: A comparative study. Bioresource Technology. 101, 624-631.
Hughes, S.R., Gibbons, W.R., Moser, B.R., Rich, J.O., (2013). Sustainable multipurpose biorefineries for third-generation biofuels and value-added co-products. in: Z. Fangs, Biofuels - economy, environment and sustainability. Published online,
Hüpfl, J., Zauner, J., (1966). Testing dissolving pulps by use of a laboratory-scale viscose plant. Papier (Paris). 20, 125-132.
Häärä, M., Sundberg, A., Willför, S., (2011). Calcium oxalate - a source of "hickey" problems - a literature review on oxalate formation, analysis and scale control. Nordic Pulp and Paper Research Journal. 26, 263-282.
Ibarra, D., Köpcke, V., Larsson, P.T., Jääskeläinen, A.-S., Ek, M., (2010). Combination of alkaline and enzymatic treatments as a process for upgrading sisal paper-grade pulp to dissolving-grade pulp. Bioresource Technology. 101, 7416-7423.
International Agency for Research on Cancer, (2013). Some chemicals present in industrial and consumer products, food and drinking-water. IARC Monographs. 101, Lyon, France.
Janson, J., (1970). Calculation of polysaccharide composition of wood and pulp. Paperi ja Puu. 52, 323-326, 328-329.
Janzon, R., Puls, J., Saake, B., (2006). Upgrading of paper-grade pulps to dissolving pulps by nitren extraction: optimisation of extraction parameters and application to different pulps. Holzforschung. 60, 347-354.
Janzon, R., Puls, J., Bohn, A., Potthast, A., Saake, B., (2008a). Upgrading of paper grade pulps to dissolving pulps by nitren extraction: yields, molecular and supramolecular structures of nitren extracted pulps. Cellulose (Dordrecht, Neth.). 15, 739-750.
Janzon, R., Saake, B., Puls, J., (2008b). Upgrading of paper-grade pulps to dissolving pulps by nitren extraction: properties of nitren extracted xylans in comparison to NaOH and KOH extracted xylans. Cellulose (Dordrecht, Neth.). 15, 161-175.

Kabel, M.A., Kortenoeven, L., Schols, H.A., Voragen, A.G.J., (2002). In vitro fermentability of differently substituted xylo-oligosaccharides. Journal of Agricultural and Food Chemistry. 50, 6205-6210.
Kamm, B., (2014). Biorefineries – their scenarios and challenges. Pure and Applied Chemistry. 86, 821-831.
Kanungo, D., Francis, R.C., Shin, N.H., (2009). Mechanistic differences between kraft and soda/AQ pulping. Part 2: Results from lignin model compounds. Journal of Wood Chemistry and Technology. 29, 227-240.
Karinen, R., Vilonen, K., Niemelä, M., (2011). Biorefining: Heterogeneously catalyzed reactions of carbohydrates for the production of furfural and hydroxymethylfurfural. ChemSusChem. 4, 1002-1016.
Karmanov, A.P., Monakov, Y.B., (2001). Hydrodynamic properties and structure of lignin. International Journal of Polymeric Materials and Polymeric Biomaterials. 48, 151-175.
Kerr, A.J., Harwood, V.D., Service, N.Z.F., (1976). Prehydrolysis-kraft pulping of New Zealand beech.
Kilpeläinen, P., Leppänen, K., Spetz, P., Kitunen, V., Ilvesniemi, H., Pranovich, A., Willför, S., (2012). Pressurised hot water extraction of acetylated xylan from birch sawdust. Nordic Pulp & Paper Research Journal. 27, 680-688.
Kilpeläinen, P.O., Hautala, S.S., Byman, O.O., Tanner, L.J., Korpinen, R.I., Lillandt, M.K.J., Pranovich, A.V., Kitunen, V.H., Willför, S.M., Ilvesniemi, H.S., (2014). Pressurized hot water flow-through extraction system scale up from the laboratory to the pilot scale. Green Chemistry. 16, 3186-3194.
Klemm, D., Philip, B., Heinze, T., Heinze, U., Wagenknecht, W., (1998). Comprehensive cellulose chemistry, Volume 1: General principles & analytical methods. WILEY-VCH Verlag GmbH, Weinheim, 300 pp.
Klemola, A., (1968). Investigations of birchwood (Betula pubescens) lignin degraded by steam hydrolysis. Suomen Kemistilehti. 41, 166-180.
Kohnke, T., Elder, T., Theliander, H., Ragauskas, A.J., (2014). Ice templated and cross-linked xylan/nanocrystalline cellulose hydrogels. Carbohydrate Polymers. 100, 24-30.
Koivula, E., Kallioinen, M., Preis, S., Testova, L., Sixta, H., Mänttäri, M., (2012). Evaluation of various pretreatment methods to manage fouling in ultrafiltration of wood hydrolysates. Separation and Purification Technology. 83, 50-56.
Kongruang, S., Han, M.J., Breton, C.I.G., Penner, M.H., (2004). Quantitative analysis of cellulose-reducing ends. Applied Biochemistry and Biotechnology. 113-116, 213-231.
Kurian, J.K., Raveendran Nair, G., Hussain, A., Vijaya Raghavan, G.S., (2013). Feedstocks, logistics and pre-treatment processes for sustainable lignocellulosic biorefineries: A comprehensive review. Renewable and Sustainable Energy Reviews. 25, 205-219.
Kuzmenko, V., Hägg, D., Toriz, G., Gatenholm, P., (2014). In situ forming spruce xylan-based hydrogel for cell immobilization. Carbohydrate Polymers. 102, 862-868.
Kämppi, R., Hörhammer, H., Leponiemi, A., Van Heiningen, A., (2010). Pre-extraction and PSAQ pulping of siberian larch. Nordic Pulp & Paper Research Journal. 25, 243-248.
Köpcke, V., Ibarra, D., Ek, M., (2008). Increasing accessibility and reactivity of paper grade pulp by enzymatic treatment for use as dissolving pulp. Nordic Pulp & Paper Research Journal. 23, 363-368.
Lai, Y.-Z., Sarkanen, K.V., (1967). Kinetics of alkaline hydrolysis of glycosidic bonds in cotton cellulose. Cellulose Chemistry and Technology. 1, 517-527.
Larsson, P.T., Wickholm, K., Iversen, T., (1997). A CP/MAS carbon-13 NMR investigation of molecular ordering in celluloses. Carbohydrate Research. 302, 19-25.

Lehtaru, J., Ilomets, T., (1996). Stabilization of cellulose fibers with sodium borohydride. Proceedings of the Estonian Academy of Sciences. Chemistry. 45, 160-168.
Lehto, J., Alen, R., (2013). Alkaline pre-treatment of hardwood chips prior to delignification. Journal of Wood Chemistry and Technology. 33, 77-91.
Lenzing.Com, http://www.lenzing.com/.
Leppänen, K., Andersson, S., Torkkeli, M., Knaapila, M., Kotelnikova, N., Serimaa, R., (2009). Structure of cellulose and microcrystalline cellulose from various wood species, cotton and flax studied by X-ray scattering. Cellulose. 16, 999-1015.
Leschinsky, M., Zuckerstätter, G., Weber Hedda, K., Patt, R., Sixta, H., (2008a). Effect of autohydrolysis of Eucalyptus globulus wood on lignin structure. Part 1: Comparison of different lignin fractions formed during water prehydrolysis. Holzforschung. 62, 645-652.
Leschinsky, M., Zuckerstätter, G., Weber Hedda, K., Patt, R., Sixta, H., (2008b). Effect of autohydrolysis of Eucalyptus globulus wood on lignin structure. Part 2: Influence of autohydrolysis intensity. Holzforschung. 62, 653-658.
Leschinsky, M., Sixta, H., Patt, R., (2009). Detailed mass balances of the autohydrolysis of Eucalyptus globulus at 170°C. BioResources. 4, 687-703.
Li, H., Saeed, A., Jahan, M.S., Ni, Y., Van Heiningen, A., (2010). Hemicellulose removal from hardwood chips in the pre-hydrolysis step of the kraft-based dissolving pulp production process. Journal of Wood Chemistry and Technology. 30, 48-60.
Li, S., Lundquist, K., Westermark, U., (2000). Cleavage of arylglycerol β-aryl ethers under neutral and acid conditions. Nordic Pulp & Paper Research Journal. 15, 292-299.
Lindberg, B., Rosell, K.G., Svensson, S., (1973). Positions of the O-acetyl groups in birch xylan. Svensk Papperstidning. 76, 30-32.
Lindenfors, S., (1980). Additives in alkaline pulping - what reduces what? Svensk Papperstidning. 83, 165-173.
Lora, J.H., Wayman, M., (1978a). Autohydrolysis-extraction: a new approach to sulfur-free pulping. Tappi. 61, 88-89.
Lora, J.H., Wayman, M., (1978b). Delignification of hardwoods by autohydrolysis and extraction. Tappi. 61, 47-50.
Lora, J.H., Wayman, M., (1980). Autohydrolysis of aspen milled wood lignin. Canadian Journal of Chemistry. 58, 669-676.
Menon, V., Rao, M., (2012). Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. Progress in Energy and Combustion Science. 38, 522-550.
Meshgini, M., Sarkanen Kyosti, V., (1989). Synthesis and kinetics of acid-catalyzed hydrolysis of some α-aryl tther lignin model compounds. Holzforschung. 43, 239-243.
Metla Finnish Forest Research Institute, (2009). Statistical yearbook of Forestry. Vantaa.
Metsagroup.Com, http://metsagroup.com/.
Metsämuuronen, S., Lyytikäinen, K., Backfolk, K., Siren, H., (2013). Determination of xylo-oligosaccharides in enzymatically hydrolysed pulp by liquid chromatography and capillary electrophoresis. Cellulose. 20, 1121-1133.
Mikkonen, K.S., Tenkanen, M., (2012). Sustainable food-packaging materials based on future biorefinery products: Xylans and mannans. Trends in Food Science & Technology. 28, 90-102.
Mwv.Com, http://http://www.mwv.com/.
Nabarlatz, D., Farriol, X., Montané, D., (2004). Kinetic modeling of the autohydrolysis of lignocellulosic biomass for the production of hemicellulose-derived oligosaccharides. Industrial & Engineering Chemistry Research. 43, 4124-4131.
Nabarlatz, D., Ebringerova, A., Montane, D., (2007). Autohydrolysis of agricultural by-products for the production of xylo-oligosaccharides. Carbohydrate Polymers. 69, 20-28.

Nanji, D.R., Paton, F.J., Ling, A.R., (1925). Decarboxylation of polysaccharide acids; Its application to the establishment of the constitution of pectins and to their determination. Journal of the Society of Chemical Industry, London. 44, 253-258T.
Niemelä, K., Tamminen, T., Ohra-Aho, T., (2008). Black liquor components as potential raw materials. Tapssa Journal. Available online http://www.tappsa.co.za/archive3/Journal_papers/Black_Liquor_Components/black_liquor_components.html,
Nigam, P., Singh, D., (1995). Processes of fermentative production of xylitol — a sugar substitute. Process Biochemistry. 30, 117-124.
Nikitin, V.M., Obolenskaya, A.V., Shchegolev, V.P., (1978). Chemistry of wood and cellulose. Lesnaya Promyshlennost, Moscow, 368 pp.
Nilsson, H.E.R., Östberg, K., (1968). Kraft pulping with the addition of hydrazine. Svensk Papperstidning. 71, 71-76.
Nrel (2009). What Is a Biorefinery? , http://www.nrel.gov/biomass/biorefinery.html.
Oksanen, T., Buchert, J., Viikari, L., (1997). The role of hemicelluloses in the hornification of bleached kraft pulps. Holzforschung. 51, 355-360.
Overbeck, W., Mülller, H., (1942). Hydrolysis of different wood species with water under pressure and the resultingchanges of the wood constituents, the lignin in particular. Bulletin of the Institute of Paper Chemistry. 13, 145.
Paananen, M., Tamminen, T., Nieminen, K., Sixta, H., (2010). Galactoglucomannan stabilization during the initial kraft cooking of Scots pine. Holzforschung. 64, 683-692.
Paananen, M., Liitiä, T., Sixta, H., (2013). Further insight into carbohydrate degradation and gissolution behavior during kraft cooking under elevated alkalinity without and in the presence of anthraquinone. Industrial & Engineering Chemistry Research. 52, 12777-12784.
Paleologou, M., Radiotis, T., Kouisni, L., Jemaa, N., Mahmood, T., Browne, T., Singbeil, D., (2011). New and emerging biorefinery technologies and products for the canadian forest industry. Journal of Science and Technology for Forest Products and Processes. 1, 6-14.
Pavasars, I., Hagberg, J., Borén, H., Allard, B., (2003). Alkaline degradation of cellulose: Mechanisms and kinetics. Journal of Polymers and the Environment. 11, 39-47.
Penttilä, P.A., Varnai, A., Leppänen, K., Peura, M., Kallonen, A., Jääskeläinen, P., Lucenius, J., Ruokolainen, J., Siika-Aho, M., Viikari, L., Serimaa, R., (2010). Changes in submicrometer structure of enzymatically hydrolyzed microcrystalline cellulose. Biomacromolecules. 11, 1111-1117.
Penttilä, P.A., Kilpeläinen, P., Tolonen, L., Suuronen, J.-P., Sixta, H., Willför, S., Serimaa, R., (2013). Effects of pressurized hot water extraction on the nanoscale structure of birch sawdust. Cellulose. 20, 2335-2347.
Pinto, P.C., Evtuguin, D.V., Neto, C.P., (2005). Effect of structural features of wood biopolymers on hardwood pulping and bleaching performance. Industrial & Engineering Chemistry Research. 44, 9777-9784.
Piteasciencepark.Se, http://www.piteasciencepark.se/.
Puls, J., Schmidt, O., Granzow, C., (1987). alpha -Glucuronidase in two microbial xylanolytic systems. Enzyme and Microbial Technology. 9, 83-88.
Puls, J., Schröder, N., Stein, A., Janzon, R., Saake, B., (2005). Xylans from oat spelts and birch kraft pulp. Macromolecular Symposia. 232, 85-92.
Puls, J., Janzon, R., Saake, B., (2006). Comparative removal of hemicelluloses from paper pulps using nitren, cuen, NaOH, and KOH. Lenzinger Berichte. 86, 63-70.
Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick, W.J., Jr., Hallett, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R., Tschaplinski, T., (2006). The path forward for biofuels and biomaterials. Science (Washington, DC, U. S.). 311, 484-489.

Rahikainen, J.L., Martin-Sampedro, R., Heikkinen, H., Rovio, S., Marjamaa, K., Tamminen, T., Rojas, O.J., Kruus, K., (2013). Inhibitory effect of lignin during cellulose bioconversion: The effect of lignin chemistry on non-productive enzyme adsorption. Bioresource Technology. 133, 270-278.

Rantanen, H., Virkki, L., Tuomainen, P., Kabel, M., Schols, H., Tenkanen, M., (2007). Preparation of arabinoxylobiose from rye xylan using family 10 Aspergillus aculeatus endo-1,4-β-d-xylanase. Carbohydrate Polymers. 68, 350-359.

Rauhala, T., King, A.W.T., Zuckerstätter, G., Suuronen, S., Sixta, H., (2011). Effect of autohydrolysis on the lignin structure and the kinetics of delignification of birch wood. Nordic Pulp & Paper Research Journal. 26, 386-391.

Richter, G.A., (1955). Production of high alpha-cellulose wood pulps and their properties. Tappi. 38, 129-150.

Richter, G.A., (1956). Some aspects of prehydrolysis pulping. Tappi. 39, 193-210.

Roselli, A. (2011). Soda-AQ cooking of alkaline pre-extracted birch wood chips. *Department of Forest Products Technology*. Aalto University, Espoo.

Roselli, A., Froschauer, C., Hummel, M., Sixta, H. (2013). IONCELL: selective xylan extraction with ionic liquids. *ISWFPC*. Vancouver, Canada.

Roselli, A., Asikainen, S., Stepan, A., Monshizadeh, A., Weymarn, N.V., Kovasin, K., Hummel, M., Sixta, H. (2014a). IONCELL-P: Selective hemicellulose extraction method with ionic liquids. *European Workshop on Lignocellulosics and Pulp*. Seville, Spain.

Roselli, A., Hummel, M., Monshizadeh, A., Maloney, T., Sixta, H., (2014b). Ionic liquid extraction method for upgrading eucalyptus kraft pulp to high purity dissolving pulp Cellulose Published online.

Rudie, A., Reiner, R., Ross-Sutherland, N., Kenealy, W., (2007). Acid Prehydrolysis of Wood.

Rydholm, S.A., (1964). Pulping processes. Interscience Publishers, John Wiley & Sons, Inc., London, 1300 pp.

Råmark, H., Leavitt, A. (2012). Andritz's new technology applied to dissolving pulp grades - a different approach. *4th Nordic Wood Biorefinery Conference*. pp. 82-86. Helsinki, Finland.

Röhrling, J., Potthast, A., Rosenau, T., Lange, T., Ebner, G., Sixta, H., Kosma, P., (2002). A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 1. Method development. Biomacromolecules. 3, 959-968.

Salak Asghari, F., Yoshida, H., (2006). Acid-catalyzed production of 5-hydroxymethyl furfural from d-fructose in subcritical water. Industrial & Engineering Chemistry Research. 45, 2163-2173.

Sarkanen, K.V., Ludwig, C.H., (1971). Lignins: occurrence, formation, structure and reactions. Wiley-Interscience, New York,

Schild, G., Müller, W., Sixta, H., (1996). Prehydrolysis kraft and ASAM paper grade pulping of eucalypt wood. A kinetic study. Das Papier. 50, 10-22.

Schild, G., Sixta, H., Testova, L., (2010). Multifunctional alkaline pulping, delignification and hemicellulose extraction. Cellulose Chemistry and Technology. 44, 35-45.

Schild, G., Sixta, H., (2011). Sulfur-free dissolving pulps and their application for viscose and lyocell. Cellulose. 18, 1113-1128.

Sears, K.D., Hinck, J.F., Sewell, C.G., (1982). Highly reactive wood pulps for cellulose acetate production. Journal of Applied Polymer Science. 27, 4599-4610.

Sedlmeyer, F.B., (2011). Xylan as by-product of biorefineries: Characteristics and potential use for food applications. Food Hydrocolloids. 25, 1891-1898.

Shallom, D., Shoham, Y., (2003). Microbial hemicellulases. Current Opinion in Microbiology. 6, 219-228.

Sihtola, H., Blomberg, L., (1974). A new method for removal of hemicelluloses from steeping lye when using low-alpha pulp with particular reference to a double-steeping viscose process. Tappi. 57, 73-75.

Silva, T.C.F., Colodette, J.L., Lucia, L.A., Oliveira, R.C.D., Oliveira, F.V.N., Silva, L.H.M., (2010). Adsorption of chemically modified xylans on eucalyptus pulp and its effect on the pulp physical properties. Industrial & Engineering Chemistry Research. 50, 1138-1145.

Sixta, H., Potthast, A., Krotschek, A.W., (2006). Chemical pulping processes. in: H. Sixtas, Handbook of pulp. WILEY-VCH, Weinheim, pp. 109-509.

Sixta, H., (2006a). Pulp properties and applications. in: H. Sixtas, Handbook of Pulp. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 1009-1067.

Sixta, H., (2006b). Pulp purification. in: H. Sixtas, Handbook of Pulp. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 933-965.

Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., Heiningen, A., Froschauer, C., Schottenberger, H., (2013). Novel concepts of dissolving pulp production. Cellulose. 20, 1547-1561.

Sjöström, E., (1989). The origin of charge on cellulosic fibers. Nordic Pulp & Paper Research Journal. 4, 90-93.

Sjöström, E., (1993). Wood chemistry: fundamentals and applications, 2nd edition. Academic Press, San Diego, 293 pp.

Springer, E.L., (1985). Prehydrolysis of hardwoods with dilute sulfuric acid. Industrial & Engineering Chemistry Product Research and Development 24, 614-623.

Stepan, A.M., King, A.W.T., Kakko, T., Toriz, G., Kilpeläinen, I., Gatenholm, P., (2013). Fast and highly efficient acetylation of xylans in ionic liquid systems. Cellulose. 20, 2813-2824.

Sundberg, A., Sundberg, K., Lillandt, C., Holmbom, B., (1996). Determination of hemicelluloses and pectins in wood and pulp fibers by acid methanolysis and gas chromatography. Nordic Pulp & Paper Research Journal. 11, 216-219, 226.

Suurnäkki, A., Heijnesson, A., Buchert, J., Tenkanen, M., Viikari, L., Westermark, U., (1996). Location of xylanase and mannanase action in kraft fibers. Journal of Pulp and Paper Science. 22, J78-J83.

Svenson, D.R., Li, J., (2005). Manufacturing high purity xylose from hemicellulose containing cellulosic material and xylose production system. US Patent 20050203291A1.

Süss, H.-U., (2008). Environmental aspects of pulp production. in: H. Sixtas, Handbook of Pulp. Wiley-VCH Verlag GmbH, Weinheim, pp. 997-1008.

Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., Vuorinen, T., (1995). Characterization of 4-deoxy-β-L-threo-hex-4-enopyranosyluronic acid attached to xylan in pine kraft pulp and pulping liquor by carbon-13 and proton NMR spectrometry. Carbohydrate Research. 272, 55-71.

Teleman, A., Tenkanen, M., Jacobs, A., Dahlman, O., (2002). Characterization of O-acetyl-(4-O-methylglucurono)xylan isolated from birch and beech. Carbohydrate Research. 337, 373-377.

Testova, L. (2006). Hemicelluloses extraction from birch wood prior to kraft cooking: extraction optimisation and pulp properties investigations. *Department of Chemical Engineering and Geosciences*. Luleå University of Technology, Luleå.

Testova, L., Vilonen, K., Pynnonen, H., Tenkanen, M., Sixta, H., (2009). Isolation of hemicelluloses from birch wood: distribution of wood components and preliminary trials in dehydration of hemicelluloses. Lenzinger Berichte. 87, 58-65.

Testova, L., Leppikallio, M., Sixta, H. (2012a). Sulfur-free production of paper-grade pulps from oxalic acid prehydrolysed birch wood. *European Workshop on Lignocellulosics and Pulp*. pp. 536-539. Espoo, Finland.

Testova, L., Roselli, A., Costabel, L., Sixta, H. (2012b). From birch to Soda-AQ pulps, pure xylan and fractions thereof - Hemiex project overview. *4th Nordic Wood Biorefinery Conference*. pp. 298-300. Helsinki, Finland.

Tolonen, L.K., Zuckerstätter, G., Penttilä, P.A., Milacher, W., Habicht, W., Serimaa, R., Kruse, A., Sixta, H., (2011). Structural changes in microcrystalline cellulose in subcritical water treatment. Biomacromolecules. 12, 2544-2551.
Treiber, E., Rehnstrom, J., Ameen, C., Kolos, F., (1962). A miniature laboratory viscose "plant" for the testing of chemical pulps. Papier (Paris). 16, 85-94.
Tunc, M.S., Van Heiningen, A.R.P., (2008). Hemicellulose extraction of mixed southern hardwood with water at 150 °C: Effect of time. Industrial & Engineering Chemistry Research. 47, 7031-7037.
Tunc, M.S., Lawoko, M., Van Heiningen, A., (2010). Understanding the limitations of removal of hemicelluloses during autohydrolysis of a mixture of Southern Hardwoods. BioResources. 5, 356-371.
Vaaler, D.a.G. (2008). Yield-increasing additives in kraft pulping: Effect on carbohydrate retention, composition and handsheet properties *Department of Chemical Engineering*. Norwegian University of Science and Technology, Trondheim.
Wallberg, O., Linde, M., Jönnson, A.-S., (2006). Extraction of lignin and hemicelluloses from kraft black liquor. Desalination. 199, 413-414.
Wallis, A.F.A., Wearne, R.H., (1990). Chemical cellulose from radiata pine kraft pulp. Appita Journal. 43, 355-357, 366.
Walton, S.L., Hutto, D., Genco, J.M., Walsum, G.P.V., Heiningen, A.R.P.V., (2010). Pre-extraction of hemicelluloses from hardwood chips using an alkaline wood pulping solution followed by kraft pulping of the extracted wood chips. Industrial & Engineering Chemistry Research. 49, 12638-12645.
Van Heiningen, A., (2006). Converting a kraft pulp mill into an integrated forest biorefinery. Pulp and Paper Canada. 107, 38-43.
Van Heiningen, A., Genco, J., Yoon, S., Tunc, M.S., Zou, H., Luo, J., Mao, H., Pendse, H., (2011). Integrated forest biorefineries - near-neutral process. ACS Symposiun Series. 1067, 443-473.
Van Loon, L.R., Glaus, M.A., (1997). Review of the kinetics of alkaline degradation of cellulose in view of its relevance for safety assessment of radioactive waste repositories. Journal of Environmental Polymer Degradation. 5, 97-109.
Wayman, M., Lora, J.H., (1979). Delignification of wood by autohydrolysis and extraction. Tappi. 62, 113-114.
Vázquez, M.J., Alonso, J.L., Domı´Nguez, H., Parajó, J.C., (2000). Xylooligosaccharides: manufacture and applications. Trends in Food Science & Technology. 11, 387-393.
Vázquez, M.J., Garrote, G., Alonso, J.L., Domímguez, H., Parajó, J.C., (2005). Refining of autohydrolysis liquors of manufacturing xylooligosaccharides: evaluation of operational strategies Bioresource Technology. 96, 889-896.
Vena, P.F., García-Aparicio, M.P., Brienzo, M., Görgens, J.F., Rypstra, T., (2013). Effect of alkaline hemicellulose extraction on kraft pulp fibers from Eucalyptus grandis. Journal of Wood Chemistry and Technology. 33, 157-173.
Werpy, T., Petersen, G., Aden, A., Bozell, J., Holladay, J., White, J., Manheim, A., (2004). Top Value Added Chemicals from Biomass. U.S.Department of Energy.
Westerberg, N., Sunner, H., Helander, M., Henriksson, G., Lawoko, M., Rasmuson, A., (2012). Separation of galactoglucomannans, lignin, and lignin-carbohydrate complexes from hot-water-extracted Norway spruce by cross-flow filtration and adsorption chromatography. BioResources. 7, 4501-4516.
Wickholm, K., Larsson, P.T., Iversen, T., (1998). Assignment of non-crystalline forms in cellulose I by CP/MAS carbon-13 NMR spectroscopy. Carbohydrate Research. 312, 123-129.
Williams, D.L., Dunlop, A.P., (1948). Kinetics of furfural destruction in acidic aqueous media. Industrial & Engineering Chemistry. 40, 239-241.
Yoon, S.-H., Tunc, M.S., Van Heiningen, A., (2011). Near-neutral pre-extraction of hemicelluloses and subsequent kraft pulping of southern mixed hardwoods. Tappi Journal. 10, 7-15.

Zeitsch, K.J., (2000). The chemistry and technology of furfural and its many by-products. Elsevier Science, Amsterdam, 376 pp.
Zhang, Y.H.P., (2013). Next generation biorefineries will solve the food, biofuels, and environmental trilemma in the energy–food–water nexus. Energy Science & Engineering. 1, 27-41.
Öhman, F., Danielsson, S. (2011). Separation of xylan from the kraft pulp mill. *3rd Nordic Wood Biorefinery Conference*. p. 85. Stockholm, Sweden.

Aalto-DD 208/2014

ISBN 978-952-60-6015-6 (printed)
ISBN 978-952-60-6016-3 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

Aalto University
School of Chemical Technology
Department of Forest Products Technology
www.aalto.fi

BUSINESS +
ECONOMY

ART +
DESIGN +
ARCHITECTURE

SCIENCE +
TECHNOLOGY

CROSSOVER

DOCTORAL
DISSERTATIONS